The Institute of Paper Science and Technology

Atlanta, Georgia

Doctor's Dissertation

Sulfur Release During the Pyrolysis of Kraft Black Liquor

Frank D. Harper

June, 1989

SULFUR RELEASE DURING THE PYROLYSIS OF KRAFT BLACK LIQUOR

A thesis submitted by

Frank D. Harper

B. S. 1977, North Carolina State University, Raleigh, N. C.

M. S. 1986, Lawrence University

in partial fulfillment of the requirements
of The Institute of Paper Chemistry
for the degree of Doctor of Philosophy
from Lawrence University
Appleton, Wisconsin

June, 1989

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ABSTRACT

Sulfur release during kraft black liquor combustion results in several significant recovery boiler problems. Much of this release occurs during the pyrolysis stage of burning, with the sulfur being released in the form of reduced sulfur compounds. Despite the importance of this phenomenon, much of the information available on sulfur release during black liquor pyrolysis is incomplete or contradictory.

The objective of this thesis was to develop a model that predicts the amount of sulfur volatilized from a black liquor drop during pyrolysis. The model was to account for the effects of important compositional and physical variables on the release of sulfur during pyrolysis.

To determine the effect of compositional variables on the amount of sulfur released, soda liquors containing a single sulfur species were pyrolyzed at temperatures between 250 and 750^{o} C in a captive sample reactor and the amount of released sulfur measured. Very little (<2%) sulfur was released during pyrolysis of liquors containing sodium sulfate or sodium sulfite. About forty per cent of the sulfur could be released from liquors containing sodium thiosulfate or sodium sulfide. Sulfur release increased with increasing temperature up to 490^{o} C. At higher pyrolysis temperatures, the amount of sulfur released decreased with increasing temperature.

Equations were developed to predict the amount of sulfur released from thiosulfate and sulfide as a function of pyrolysis time and temperature. These equations describe sulfur release using a modified first order

decomposition model. The results of the study show that, although the amount of sulfur that can be released from either sodium thiosulfate or sodium sulfide is similar, the thiosulfate release rate is much lower.

The relationships between the physical parameters of a black liquor drop and the transfer of heat to and through the drop during pyrolysis were determined. Drops of varying size, solids contents, and swelling characteristics were pyrolyzed and measurements made of their external and internal temperatures. These temperature measurements were used to develop a heat transfer model which predicts a black liquor drop's temperature. The model assumes that external heat transfer controls the rate of temperature increase and that the drop swells linearly with temperature between 250 and 500 degrees C. In the model, the black liquor drop is divided into three equal-mass, isothermal layers.

The kinetic and heat transfer models were combined to produce a model that predicts the amount of sulfur that will be released from a pyrolyzing black liquor drop as a function of the drop's physical characteristics, its sulfur composition, and the heating environment to which it is exposed. Predictions from the model were compared with sulfur releases obtained from pyrolysis tests of actual black liquor drops. The model was also used to predict changes in sulfur release that would result from oxidizing the liquor, which converts the liquor's sulfide to thiosulfate. Because of thiosulfate's lower sulfur release rate, lower sulfur releases can be obtained by oxidation of kraft black liquor.

INTRODUCTION

The kraft pulping process is the dominant method for producing chemical pulp in the United States. Approximately ninety per cent of the nation's chemical pulp is produced by the kraft process[1]. One of the reasons for kraft's dominance is its recovery system, which allows its primary cooking chemicals, sodium hydroxide and sodium sulfide, to be recycled.

After pulping is completed, the wood fibers, or pulp, are separated from the dissolved wood components and the spent cooking chemicals by washing. This mixture of dissolved wood and spent chemicals, called black liquor, is usually removed from the washers at about fourteen to seventeen per cent solids. The black liquor is then sent to evaporators where it is concentrated to a level of about sixty-five per cent solids. From there, it is sprayed into the recovery boiler where the organic portion of the liquor is burned and the inorganic chemicals, consisting chiefly of sodium carbonate and sodium sulfide, are melted and removed from the boiler. The carbonate and sulfide are then dissolved and mixed with calcium hydroxide to convert the sodium carbonate to sodium hydroxide. The calcium carbonate formed in this process is separated from the liquor and the resulting hydroxide-sulfide solution is ready for use as a pulping reagent.

The centerpiece of the recovery process is the kraft recovery boiler. This large, complex piece of equipment has two primary functions: to recover the cooking chemicals used to produce the pulp, and to produce process steam by burning the dissolved organic components. Although the recovery boiler performs these functions quite well, there are some serious problems

associated with its operation. One of these problems is sulfur release, chiefly in the form of reduced sulfur gases, during black liquor combustion. These gases, which result in an odor problem if released from the boiler, can also react with oxygen to form sulfur dioxide. The presence of SO_2 in the boiler can result in additional problems such as an increase in formation of sticky deposits in the boiler's convective heat recovery section, and corrosion throughout the boiler[2].

Much of the sulfur dioxide formed during black liquor burning can be recaptured. The SO_2 can react with fume and oxygen in the furnace's upper zones to form sodium sulfate. Fume is believed to originate as sodium vapor produced by reactions that occur during char burning or smelt reoxidation[3]. The sodium sulfate thus produced can then be trapped in the boiler's electrostatic precipitator and returned to the furnace by mixing it with the incoming black liquor. This process, however, necessitates a high particulate recycle rate. Reducing the amount of sulfur released from the burning liquor might allow a decrease in the amount of fume produced, as less would be needed to maintain the proper conditions in the upper furnace.

Despite the importance of the sulfur release phenomenon, many of the parameters that affect it are not well understood. In addition, much of the information that has been published on sulfur release is incomplete, and, in some cases, contradictory. Thus, a more systematic and complete study of sulfur release during kraft black liquor burning would aid the understanding and the control of this phenomenon.

LITERATURE REVIEW

BLACK LIQUOR COMPOSITION

Kraft black liquor is a viscous, dark brown liquid that is formed as a by-product of the kraft pulping process. During a kraft cook a solution of sodium hydroxide and sodium sulfide is used to dissolve certain wood components. An elemental analysis of black liquor solids resulting from a typical softwood kraft pulping process is shown in Table 1.

Table 1. Elemental analysis of a typical softwood kraft black liquor[4].
Weight Per Cent of Dry Liquor Solids

Element	Weight %
Carbon	38.8
Hydrogen	3.9
Oxygen	35.2
Sulfur	3.4
Sodium	18.7

Approximately one half of the wood is dissolved during the pulping process. Most of the dissolved wood originates from the hemicellulose and lignin fractions, with lesser amounts coming from cellulose and extractives. The composition of a typical softwood kraft black liquor is shown in Table 2.

The sulfur contained in the kraft black liquor may be present in several sulfur species. The largest of these is either sodium sulfide (Na_2S) or sodium thiosulfate ($Na_2S_2O_3$), depending on whether or not the liquor has been subjected to black liquor oxidation. In black liquor oxidation, air or oxygen is used to convert the liquor's sulfide to thiosulfate. This process is generally employed in operations that use a direct contact evaporator to

Table 2. Composition of a typical softwood kraft black liquor[5].
Weight Per Cent of Dry Solids

Component	Weight %
Alkali Lignin	30-35
Hydroxy Acids	25-35
Extractives	3-5
Acetic Acid	5
Formic Acid	3
Methanol	1
Sulfur	3-5
Sodium	15-20

concentrate liquor. In direct contact evaporators, hot flue gases are used to evaporate the liquor. Oxidation of the liquor prevents stripping of sulfur from the liquor in the form of reduced sulfur gases[6].

Other inorganic sulfur compounds that may be present in black liquor include sodium sulfate (Na_2SO_4) and sodium sulfite (Na_2SO_3). Some sodium thiosulfate will also be present in unoxidized liquor. These four sulfur-containing species usually account for eighty to ninety per cent of the black liquor's total sulfur[7,8,9,10]. Most of the remainder of the liquor's sulfur content is believed to be chemically bound to the lignin fraction of the liquor, and is generally referred to as organic sulfur[8]. The amount of organic sulfur contained in a black liquor is usually estimated as the difference between the sum of the four inorganic sulfur species mentioned above and the total sulfur content. Analysis of a kraft lignin showed it to be about 2.5% sulfur[11]. Table 3 gives the results of sulfur analyses of three kraft liquors used in this study. The table shows the fraction of the total sulfur contained as sulfate, sulfite, thiosulfate, and sulfide.

Table 3. Analysis of sulfur content of kraft black liquors.
(As per cent of black liquor solids)

Total Sulfur	3.35	3.37	4.28
Sulfur in			
1. SO_4^{2-}	0.50	0.37	0.70
2. SO_3^{2-}	0.40	0.24	0.32
3. $S_2O_3^{2-}$	1.37	2.14	0.80
4. S^{2-}	0.59	0.33	2.08
Sum of (1-4)	2.86	3.08	3.90
Sum as % of Total Sulfur	85.4	91.4	91.1

SULFUR RELEASE DURING BLACK LIQUOR COMBUSTION

Burning Stage of Sulfur Release

The combustion of a black liquor drop in a recovery boiler can be divided into four stages. The first of these stages is drying, during which the water remaining in the drop is evaporated. During drying the drop swells and its surface ruptures as a result of boiling. The second stage of burning is pyrolysis, which is the irreversible degradation of the organic portion of the liquor caused by thermal effects. During pyrolysis, the liquor drop swells to many times its original volume as gaseous pyrolysis products are produced. These gaseous products are subsequently burned. The part of the black liquor that is not gasified during pyrolysis is known as char. Kraft liquor char is composed of sodium salts and carbon. During the third stage of burning the carbon is gasified to form CO and CO_2 and the inorganic compounds are melted. Much of the char burning occurs on the furnace's char bed, where the sodium sulfate present in the liquor can be reduced to sodium sulfide and be removed

from the boiler along with the rest of the molten salts. The final phase of burning consists of the inorganic reactions that occur after the drop's carbon matrix is gasified[12].

Pyrolysis reactions in black liquor occur after the liquor has dried and temperatures reach 200° C or higher. Miller[13], studying the pyrolysis behavior of black liquor, found that black liquor solids, when heated, began to form bubbles at a temperature of about 240 degrees C, signaling the onset of pyrolysis. Black liquor studies using gas chromatographs to analyze the gases produced by thermogravimetric analysis (TGA) show sulfur release beginning at temperatures above 200° C[14], and it is generally agreed that most of the sulfur volatilized during black liquor combustion occurs during the pyrolysis stage of black liquor burning[5].

Beckworth et al.[15] used thermogravimetric analysis (TGA) to study the decomposition of kraft black liquor and lignin. Ten milligram samples of fifty-five per cent solids kraft black liquor were heated in the TGA apparatus in nitrogen at a heating rate of ten degrees C per minute. TGA curves of several different black liquors had similar shapes. Based on the curves obtained, the researchers divided the decomposition of black liquor into four characteristic regions. The first region, from ambient temperature to 200° C, was called the drying region, as water was the major gaseous product evolved. The second region, from 200 to 500 degrees C, was characterized by weight loss due to the decomposition of organic material. Mercaptans were emitted over this region (as detected by smell). The third region ranged between 500 and 900° C. In this region the weight remained constant until the temperature reached 650 degrees C. It was believed that at temperatures greater than 650,

the carbon reacted with the sodium sulfate in the char, reducing it to sulfide. The residue remaining at 900° C was white and water soluble, and was believed to consist mainly of sodium salts. Above 900° C, sodium vapor was given off as the salts began to decompose and vaporize.

Samples of a precipitated lignin were also analyzed using TGA. The shape of the weight loss curve obtained from lignin was similar to that obtained from black liquor in the 200 to 500 degree C range. Because of the curves' similar shapes, Beckworth et al.[15] concluded that lignin was the material in black liquor being decomposed in the 200 to 500° C range.

Some of the results reported by Beckworth et al.[15] are unexpected. They found that the residue remaining after pyrolysis was complete was composed chiefly of water soluble inorganic salts. However, for black liquor samples that are pyrolyzed in an inert atmosphere, there should be large amounts of carbon remaining as char after pyrolysis is complete. For the organic portions of the liquor to completely gasify, it is necessary to react the char with oxygen or an oxygen-containing compound (such as CO_2). In view of the results reported, it seems probable that there was air leakage in the reactor. Also, it was reported that the sodium vapor observed resulted from decomposition and vaporization of the liquor's inorganic salts. However,the salts present in black liquor: sodium carbonate, sodium sulfide, and sodium sulfate, are all stable at 900° C in a nitrogen atmosphere.

Li[14] also used thermogravimetric analysis to study the pyrolysis behavior of black liquor. Black liquor solids were heated in a TGA apparatus at a rate of twenty degrees C per minute until a final temperature of 700 to 800° C was

reached. The pyrolysis took place in an atmosphere of pure helium or a mixture of helium and carbon monoxide (~12% CO). The gases produced by the pyrolysis were analyzed by gas chromatography.

Release of sulfur gases from the liquor began at temperatures greater than 200 degrees C. The major sulfur-containing species were dimethyl sulfide (49% of total released sulfur), methyl mercaptan (28%), and hydrogen sulfide (18%). A small amount of dimethyl disulfide (4%) was also produced. The emission of sulfur-containing gases had ended by the time a temperature of 460° C had been reached. No additional sulfur release was observed during the heating of the solids to a final temperature of 750 degrees C. When CO was added to the helium, a small amount (1% of total volatilized sulfur) of carbonyl sulfide (COS) was produced at temperatures greater than 550° C. The total amount of sulfur released was about twenty-two per cent of the liquor solids' total sulfur content.

Effect of Physical Variables

Process operating variables have been shown to influence the amount of sulfur that is volatilized during black liquor combustion. These effects have been observed in both pyrolysis and burning studies. The process parameters that affect sulfur release include pyrolysis temperature, particle size, and solids content.

Feuerstein et al.[16] studied the pyrolysis of kraft black liquor in a batch reactor. Black liquor samples (65% solids) were slowly heated to final temperatures ranging from 398 to 970° C. The pyrolysis products were separated into four fractions: the solid pyrolysis residue, a water fraction

removed from the gas stream by a condenser, an organic liquid fraction removed from the gas by an aerosol trap, and the noncondensable pyrolysis gases. The concentrations of the gases produced were then measured. Total pyrolysis gas production increased from approximately five per cent of total black liquor solids at 398° C to about fifteen per cent of the total solids weight at 970°. The major non-sulfur gaseous products observed were hydrogen, methane, ethane, acetylene, carbon monoxide, and carbon dioxide. The yields of the hydrocarbon products remained constant with increasing temperature once their maximum values were reached while the amounts of CO, CO_2 and H_2 increased throughout the temperature range studied.

The products of pyrolysis were analyzed for sulfur content. The solid pyrolysis char contained 20 to 40% of the total sulfur, depending on the temperature to which the liquor was heated. The presence of over twenty sulfur-containing species was detected in the organic liquid fraction. The pyrolysis liquid, however, contained only a small fraction of the liquor's sulfur (<10%). The water fraction also contained only minor amounts of sulfur (about 5% of total). Most of the sulfur (60 to 70%) was volatilized to gaseous products, the most prevalent of which were hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The amount of total sulfur volatilized increased with increasing final temperature up to levels of about 675° (but thereafter decreased). The hydrogen sulfide yield increased with increasing temperature, while the amounts of methyl mercaptan and dimethyl sulfide remained constant or decreased as the final temperature was raised. Dimethyl disulfide appeared only at higher temperatures (>600° C) with its level remaining essentially constant at temperatures above 600° C.

Based on analysis of the condensed products, it was estimated that the amount of sulfur in the gas fraction reached a maximum of over seventy per cent of the liquor's original sulfur content at a temperature of 675° and decreased to less than sixty per cent at 970°. At temperatures typical of those found in recovery furnaces, about seventy per cent of the sulfur was volatilized.

Pyrolysis of black liquor was examined by Jones[17] using a continuous reactor. Black liquor samples were injected into a reactor that had been heated to levels ranging from 580 to 1135° C. The resulting pyrolysis gases were captured and analyzed. Brink et al.[18] compared Jones' results to those obtained by Feuerstein et al.[15]. Above temperatures of 500° C the volumes of gases produced by the continuous reactor far exceeded the amount of gas volatilized in the batch reactor. At high temperatures (1000° C) the continuous reactor produced gas volumes that were five times those produced by the batch reactor. The composition of the gases produced also differed for the two reactors, with much more H_2, CO, and CO_2 being produced in the continuous reactor.

The differences in gas production observed was attributed to the differences in the amounts of water vapor present in the two reactors[18]. In the batch reactor, steam that is produced during the drying or pyrolysis of the liquor is quickly removed from the system by the purge gas. Consequently, little water vapor is available at higher temperatures to gasify carbon by the reaction:

$$C + H_2O \Rightarrow CO + H_2. \qquad (1)$$

More steam is available in the continuous reactor at all temperatures as wet liquor is injected directly into an already heated reactor. The presence of

water vapor in the continuous reactor also accounts for the difference in CO/CO_2 ratios observed in the two reactors. In the batch reactor the concentration of CO is equal to or greater than that of CO_2 throughout the temperature range examined. In the continuous reactor, however, the concentration of carbon dioxide exceeded that of carbon monoxide. The ratio of CO to CO_2 is controlled by the reaction:

$$CO + H_2O \Rightarrow CO_2 + H_2. \qquad (2)$$

Thus, the continuous reactor contains the water necessary to drive reaction (2) to the right.

The amounts of sulfur volatilized by the two reactors was also compared[18]. In the continuous reactor, the amount of sulfur released to the gas phase decreased from about 75 per cent at a pyrolysis temperature of 580 degrees to about 30 per cent at temperatures above 1000°. The types of sulfur-containing gases released also varied in a manner that was dependent on the type of reactor used. During batch reactor pyrolysis, H_2S concentration increased steadily with increasing temperature. The concentrations of CH_3SH, CH_3SCH_3, and CH_3SSCH_3 reached a maximum at temperatures of 500, 600, and 800 degrees respectively. On the other hand, pyrolysis in the steady state reactor resulted in the H_2S concentration reaching a maximum at 750° C. The concentrations of CH_3SH, CH_3SCH_3, and CH_3SSCH_3 were all at their highest level at the lowest temperature tested; at higher pyrolysis temperatures the amounts of these gases detected fell rapidly. Table 4 shows a comparison of the amounts and distribution of sulfur gas released from the two reactors at a single pyrolysis temperature.

Table 4. Comparison of batch and continuous pyrolysis[18]. (grams of sulfur per 100 grams of black liquor solids)

	Batch (778° C)	Continuous (755° C)
H_2S	.846	1.70
CH_3SH	.576	.167
CH_3SCH_3	.580	.258
CH_3SSCH_3	.078	.007
Other S Containing Organics	.012	.015
Water Phase	.074	--
Pyrolysis Residue	.830	1.46
Total Recovered	2.99	3.61
Original S Content	3.01	3.80

Other researchers have reported results similar to those found by Jones using a variety of experimental reactors. Bhattacharya et al.[19], using a fixed bed reactor and pyrolyzing black liquor solids at temperatures ranging from 590 to 740° C, observed decreasing H_2S release with increasing temperature throughout the temperature range studied. Fallavollita[20], who pyrolyzed black liquor solids in a fluidized bed reactor at temperatures between 500 and 700 degrees C, also found the amounts of sulfur-containing gases that were released declined with increasing temperature. Clay et al.[21] used a single particle reactor to study pyrolysis of black liquor droplets at temperatures ranging from 300 to 1100° C. They found that sulfur release to the gas phase reached a maximum at gas temperatures between 450 and 600 degrees C.

Cantrell[22] studied the effect of particle size and solids content on the amount of sulfur released from particles that were burned in air. Black liquor drops having initial diameters of one to four millimeters and ranging in solids content from 63.3% to 98.9% were studied. As particle size or

solids content increased the amount of sulfur released during burning decreased, with drop size having the larger impact. Cantrell theorized that the reason for the decline in sulfur release observed in larger particles was the formation of a liquid smelt layer on the outside of the drops during burning. This liquid smelt layer captured the sulfur being released by the inside of the drop.

On the other hand, Bhattacharya et al.[19] reported no significant difference in the amount of sulfur released during pyrolysis from black liquor solids of three different particle sizes (0.25 - 0.55 mm, 0.18 - 0.25 mm, and 0.10 - 0.18 mm). However, these particle sizes are much smaller than typical black liquor drops (as measured in a laboratory spray study[22]). Also the sample used by Bhattacharya et al. was confined in a sample cup during pyrolysis. Therefore, it cannot be concluded that changing the particle size will not affect the amount of sulfur released during pyrolysis.

Some field trials on operating recovery boilers have tested the effects of changes in physical variables on sulfur release. However, it should be noted that many of these studies measure only the gaseous sulfur emitted from the boiler itself, which most likely does not accurately reflect the amount of sulfur actually being released by the burning black liquor.

In general, tests on recovery boilers have confirmed the results of lab-scale studies on the effects of increased temperature, higher solids, and larger drops on sulfur emission. Lang et al.[24] found that any change in boiler operation that would tend to increase the lower furnace temperature, such as increasing liquor solids content, decreasing combustion air moisture

content, or increasing combustion air temperature, resulted in lower sulfur emission. Pantser[25] also reported a decrease in sulfur emissions when the lower furnace temperature is raised. Borg et al.[26] measured sulfur released from various locations on a boiler's char bed. Recovery boiler gases were sampled by a cooled probe inserted through access doors in the furnace walls. The gases were quickly cooled to about 120° C, which minimized gas reaction while preventing water condensation. The dust and water vapor in the samples were then removed and the conditioned sample was analyzed for sulfur content by a gas chromatograph[27]. Borg et al. reported that most of the sulfur volatilized came from localized cool spots on the bed. Thoen et al.[28] reported that increasing the size of the drops in the liquor spray resulted in lower sulfur emission from a recovery boiler. However, Thoen et al. credited less entrainment of liquor in the flue gas, rather than any difference in the actual amount of sulfur volatilized, for the observed decrease.

Effect of Compositional Variables

The sulfur species contained in the black liquor may also influence the amount of sulfur that is volatilized during black liquor combustion. Sulfur is present in a wide variety of compounds in black liquor, and it would be expected that these compounds would react differently during the burning processes.

Feuerstein[29], in his pyrolysis experiments, used both oxidized and unoxidized black liquor samples. The oxidized liquor was prepared by bubbling air through samples of weak (15%) black liquor. He reported no significant differences in the amounts of the pyrolysis products produced as a result of oxidation. The composition of the pyrolysis gas, however, did change.

Oxidation of the black liquor resulted in an increase in CO_2 content and a decrease in the amount of CO in the pyrolysis gas. This difference was more pronounced at lower temperatures. No significant differences in sulfur distribution among the gaseous and condensed products as a result of liquor oxidation were reported.

Jones[17], in addition to her studies of kraft black liquor pyrolysis, also tested some samples of soda liquor to which sodium sulfide or sodium sulfate had been added. The sodium sulfide-containing liquor released sulfur in amounts that were comparable to that released from kraft liquor. Very little sulfur was released from soda liquor containing sodium sulfate.

Douglas and Price[30] pyrolyzed sodium sulfate, sodium sulfite, sodium thiosulfate, sodium sulfide, and elemental sulfur in the presence of glucose and soda lignin at 600° C. The hydrogen sulfide emitted during the pyrolysis was captured by passing the pyrolysis gas through a solution of acidified cadmium chloride, and the amount of precipitated cadmium sulfide was determined. They found that little or no H_2S was emitted from the sodium sulfate or the sodium sulfite. However, large amounts of H_2S were given off during the pyrolysis of sodium thiosulfate, sodium sulfide, and elemental sulfur. The results of their experiments are shown in Table 5.

Strohbeen and Grace[31] also studied sulfur emission from inorganic sulfur species during pyrolysis with organic compounds. Sodium sulfate, sodium sulfite, sodium thiosulfate, and sodium sulfide were heated to a temperature of 550° C in the presence of sodium gluconate and vanillic acid and the amounts of the sulfur volatilized were measured. Like Douglas and Price,

Table 5. Pyrolysis of inorganic sulfur species with model compounds at 600° C.[30]
Millimoles of H_2S Produced

	Blank	Na_2SO_4	Na_2SO_3	$Na_2S_2O_3$	Na_2S	S
Soda Lignin	0.004	0.004	0.015	0.786 0.736	0.370	0.750
Glucose	0.004	0.004	0.064	1.456 1.523 1.500 1.517	0.605	0.348
Theoretical Maximum	0.0	1.00	1.00	2.00	1.00	1.00

Strohbeen and Grace found that only small amounts of sulfur were released from Na_2SO_4 or Na_2SO_3 and larger amounts from $Na_2S_2O_3$ and Na_2S. The relative amounts of sulfur released from the latter two compounds were found to differ from the results reported by Douglas and Price. While Douglas and Price found similar amounts of sulfur being released during pyrolysis of $Na_2S_2O_3$ and Na_2S, Strohbeen and Grace found that the release of sulfur during pyrolysis of sodium thiosulfate was about one third to one half of the amount of sulfur volatilized during sodium sulfide pyrolysis. Table 6 summarizes the results of these experiments.

The reasons for the differing results found by Douglas and Price and Strohbeen and Grace are not clear. One explanation offered was that the sulfide samples tested by Douglas and Price had been oxidized prior to testing with the sulfide being converted to thiosulfate[5]. Another possible explanation is that the differing amounts of sulfur volatilized result from the different organic substrates used[31].

Recovery boiler studies have also examined the effect of black liquor oxidation on the amount of sulfur volatilized. Thoen et al.[28] reported no

Table 6. Pyrolysis of inorganic sulfur compounds with model organic compounds[5].
Per cent of sulfur volatilized; based on solids analysis
(95% Confidence Intervals)

	Na_2SO_4	Na_2SO_3	$Na_2S_2O_3$	Na_2S
Vanillic Acid	-13.8 - -0.6	2.9 - 16.1	36.5 - 44.1	91.8 - 101.1
Sodium Gluconate	-8.6 - 4.5	-1.8 - 11.3	26.6 - 30.2	85.3 - 94.6

significant differences in H_2S emission from recovery boilers resulting from use of oxidized liquor. This conclusion was based on the comparison of hydrogen sulfide release from two boilers, one of which burned unoxidized liquor, the other liquor that had been oxidized. Murray[32], who measured H_2S concentrations in the flue gas leaving a recovery boiler economizer when the boiler was alternately burning oxidized and unoxidized black liquor, also observed no significant change in hydrogen sulfide concentration.

The contribution of organic sulfur to the overall amount of sulfur released from kraft black liquor during pyrolysis is not well understood. It is generally assumed that essentially all the organic sulfur is volatilized as H_2S[7,33], but experimental verification of this supposition is lacking. Li[14] found that most of the sulfur released during his TGA pyrolysis experiments was in the form of methyl mercaptan and dimethyl sulfide, with less than 20% of the total being hydrogen sulfide. Li concluded that most of this volatilized sulfur originated as organic sulfur and that about one-half of the organic sulfur was released during pyrolysis. However, this conclusion is questionable as Li's analysis of inorganic sulfur content in his liquor sample is incomplete. Also, the fraction of organic sulfur reported, about one-half

of the liquor's total sulfur content, is much higher than the ten to twenty per cent of total black liquor sulfur that is usually reported as organic sulfur[7].

Analysis of Sulfur Release Studies

Large amounts of sulfur can be volatilized from black liquor during pyrolysis. Laboratory studies of black liquor pyrolysis have shown that most of this sulfur is released as reduced sulfur compounds, such as H_2S, CH_3SH and CH_3SCH_3, with the proportion of hydrogen sulfide increasing as pyrolysis temperatures are increased[18]. These findings concur with those observed in recovery boilers, and Borg et al.[26] have concluded that all sulfur volatilized in recovery boilers is released as hydrogen sulfide (rather than SO_2).

The amount of sulfur that is released is affected by the conditions under which the liquor is pyrolyzed. The studies discussed above are in general agreement that sulfur release from kraft black liquor is suppressed at high temperatures. However, the temperature at which sulfur release begins to decline in unknown. Most of the evidence gathered to date suggests that the decline begins at temperatures in the range of 500-600^{o} C.

From the results of Cantrell[22] and studies done on operating recovery boilers[24-26,28], it may be concluded that increasing particle size and liquor solids content lowers the amount of sulfur released during black liquor combustion. It should be noted, however, that these results may not be directly applicable to sulfur release during pyrolysis. Although pyrolysis is a stage of black liquor combustion, burning is a much more complex process than is pyrolysis. Burning a liquor drop in air means that oxidation

reactions, in addition to pyrolytic decomposition reactions, will be taking place. Also, the temperature of the liquor drop during burning may be much higher than during pyrolysis as the drop receives heat from combustion of the released volatiles. These differences will result in a different product mix and may influence the amount of sulfur released by the drop.

It is agreed that the sulfur compounds present in the black liquor affect the amount of sulfur volatilized. Several studies[17,30,31] have shown that little sulfur gas results from pyrolysis of sodium sulfate or sodium sulfite. However, there is considerable disagreement in the literature as to whether oxidation of the black liquor, which converts the liquor's sulfide to thiosulfate, would affect the amount of sulfur released during pyrolysis. Strohbeen and Grace[31] report about twice as much sulfur being volatilized during pyrolysis of sodium sulfide as results from sodium thiosulfate pyrolysis. On the other hand, Feuerstein[29] reports no significant difference in the amounts of sulfur volatilized when oxidized and unoxidized liquors are pyrolyzed. However, no analysis of the sulfur species contained in the liquor prior and subsequent to his oxidation procedure is given; therefore it cannot be ascertained how much of his original liquor's sulfur content was converted from sulfide to thiosulfate. Douglas and Price[30] reported that similar amounts of sulfur were volatilized from both sulfide and thiosulfate when these sulfur species were pyrolyzed in the presence of soda lignin and glucose. It might be argued that by measuring only H_2S, Douglas and Price may have missed some of the sulfur that is released as other compounds such as mercaptans. However, considering the fact that Douglas and Price's experiments employed a high heating rate and a relatively high temperature

(600°C), H_2S should have been the dominant volatilized species.

Studies comparing combustion of oxidized and unoxidized liquors in recovery boilers have also noted no significant differences in sulfur released with oxidation[28,32]. However, the two studies reported based their conclusions on measurements made of H_2S being emitted from the boiler. This measurement is a poor indication of the amount of sulfur gas being generated in the boiler, as a properly operating recovery boiler should emit almost no hydrogen sulfide, regardless of the liquor's oxidation state. A better indication of the amount of sulfur being generated by liquor burning is the sum of the gaseous sulfur compounds emitted from the boiler (including both reduced and oxidized species) and the sulfur found in the precipitator dust.

REACTIONS OF BLACK LIQUOR SULFUR SPECIES

Sodium Sulfide Reactions

Sodium sulfide is known to release large amounts of sulfur during pyrolysis. It is generally assumed to release sulfur during black liquor pyrolysis according to the reaction:

$$Na_2S + CO_2 + H_2O \Rightarrow Na_2CO_3 + H_2S.^{5} \quad (3)$$

Kubelka and Votoupal[34] also suggest that the following reactions, which involve Na_2S, may contribute to the sulfur release from black liquor.

$$2NaOH + Na_2S + 2CO_2 \Rightarrow 2Na_2CO_3 + H_2S \quad (4)$$

$$Na_2S + 2H_2O \Rightarrow 2NaOH + H_2S \quad (5)$$

$$Na_2S + H_2O + C \Rightarrow Na_2 + H_2S + CO. \quad (6)$$

However, these reactions are not considered to be important in producing gaseous sulfur compounds. Kubelka and Votoupal state that reaction (4) is

unlikely to occur as they believe that the carbon dioxide will preferentially react with the liquor's sodium hydroxide to form sodium carbonate rather than reacting with the sodium sulfide. Reactions (5) and (6) are endothermic[35] and have equilibrium constants that are unfavorable to the formation of hydrogen sulfide at a typical furnace temperature of 1100° C[32]. Also, as these reactions are more thermodynamically favored at higher temperatures, it is unlikely that they are important since pyrolysis studies report sulfur release decreasing as temperature increases.

Jones[17] suggests that the reduced sulfur gases formed during pyrolysis result from the reaction of Na_2S with pyrolysis products and that the production of H_2S may involve intermediate species such as methyl mercaptan and dimethyl sulfide. She proposed the following reaction sequence for formation of reduced sulfur species:

$$2Na_2S + C_2H_4 + 2CO_2 + 2H_2O \Rightarrow 2CH_3SH + 2Na_2CO_3 \quad (7)$$

$$2CH_3SH + C_2H_4 \Rightarrow 2CH_3SCH_3 \quad (8)$$

$$2CH_3SH + CH_3SCH_3 \Rightarrow 2C_2H_4 + 3H_2S \quad (9)$$

$$2CH_3SH \Rightarrow C_2H_4 + 2H_2S. \quad (10)$$

This reaction sequence accounts for the fact that other reduced sulfur species, in addition to hydrogen sulfide, are formed during pyrolysis of Na_2S. However, considering the number of reactants present in reaction (7), this reaction is a composite of several reactions.

Other possible reactions resulting in release of sulfur gases from Na_2S, reported by Strohbeen[5] are:

$$Na_2S + 2CO_2 \Rightarrow Na_2CO_3 + COS \quad (11)$$

$$Na_2S + 2HCO_2H \Rightarrow Na_2CO_3 + H_2S + CH_2O. \quad (12)$$

Both of these reactions are exothermic and are thermodynamically favorable to the production of gaseous sulfur species.

Sodium Thiosulfate Reactions

The release of sulfur from sodium thiosulfate has been theorized to result from a variety of reactions. Strohbeen[5] described sulfur release from sodium gluconate and vanillic acid in terms of three reactions, two of which compete at low temperatures, the other occurring at higher temperatures. The two low temperature reactions are:

$$Na_2S_2O_3 + CO_2 \Rightarrow Na_2CO_3 + SO_2 + S \quad (13)$$

$$Na_2S_2O_3 + 3CO \Rightarrow Na_2S + S + 3CO_2. \quad (14)$$

The high temperature reaction is:

$$4Na_2S_2O_3 \Rightarrow 3Na_2SO_4 + Na_2S_5. \quad (15)$$

The sodium sulfide and the elemental sulfur produced by the above reactions can react further to form reduced gaseous sulfur compounds. Reaction (13) is probably not important in sulfur release from kraft black liquor as it requires acidic conditions. Most pyrolysis studies of kraft liquors report no SO_2 being produced.

Kubelka and Votoupal[34] reported a series of reactions to explain the behavior of thiosulfate in a recovery boiler. Sodium thiosulfate begins to decompose at 225° C according to the reaction:

$$4Na_2S_2O_3 \Rightarrow 3Na_2SO_4 + Na_2S_5. \quad (16)$$

This reaction is complete at 470° C. Na_2S_5 melts at 251.8° C. Above this temperature the sulfur is converted to Na_2S_4 and elemental sulfur. Na_2S_4 melts at 275° C and decomposes at higher temperatures to form Na_2S and elemental sulfur. Thus, the overall reaction is:

$$4Na_2S_2O_3 \Rightarrow 3Na_2SO_4 + Na_2S + 4S \quad (17)$$

with the possibility of the sulfide and sulfur reacting to form volatile sulfur compounds. Other reactions that could result in formation of volatile sulfur species from thiosulfate are[5,34]:

$$Na_2S_2O_3 \Rightarrow Na_2SO_3 + S \quad (18)$$

$$Na_2S_2O_3 + H_2O \Rightarrow Na_2SO_4 + H_2S. \quad (19)$$

$$Na_2S_2O_3 + CO_2 \Rightarrow Na_2SO_4 + COS \quad (20)$$

$$Na_2S_2O_3 + CO \Rightarrow Na_2SO_3 + COS \quad (21)$$

$$Na_2S_2O_3 + 2HCO_2H \Rightarrow 2NaHCO_3 + SO_2 + S + H_2O. \quad (22)$$

As black liquor pyrolysis studies have reported little or no production of COS or SO_2, reactions 20, 21, and 22 are probably not major contributors to the total sulfur release.

It has been shown that sodium thiosulfate will react with molten sodium carbonate to form sodium sulfide and sodium sulfate according to the reaction

$$Na_2S_2O_3 + Na_2CO_3 \Rightarrow Na_2S + Na_2SO_4 + CO_2 \quad [36]. \quad (23)$$

In molten smelt systems this reaction is extremely rapid. However, it is not known if this reaction will proceed at lower temperatures when sodium carbonate is in its solid form.

Reactions of Sodium Sulfate and Sodium Sulfite

Sodium sulfate and sodium sulfite are usually considered to be stable under pyrolysis conditions[7]. However, some release of sulfur from sulfate has been reported by Strohbeen and Grace[31], while both Strohbeen and Grace and Douglas and Price[30] reported sulfur being volatilized during sodium sulfite pyrolysis with model compounds.

Kubelka and Votopal[34] state that Na_2SO_3 decomposes at 150° C to form Na_2SO_4 and Na_2S in a three to one sulfate to sulfide ratio. The sulfide thus formed could react to form volatile sulfur compounds. However, Strohbeen[5] reported that the sulfur remaining in the char after pyrolysis of sodium sulfite with sodium gluconate and vanillic acid at 550° C was still in the form of sulfite.

Other reactions reported by Kubelka and Votoupal[34] that could result in sulfur release from sodium sulfite are:

$$Na_2SO_3 + H_2O \Rightarrow SO_2 + 2NaOH \quad (24)$$

$$Na_2SO_3 + CO_2 \Rightarrow SO_2 + Na_2CO_3. \quad (25)$$

These reactions, however, have equilibrium constants that make them favorable only at very high (1000° C) temperatures[34]. As sodium sulfite is highly unstable in the recovery furnace[37], and should exist in only minor quantities at the high temperatures typical of recovery furnaces[38], reactions (24) and (25) should not contribute significantly to sulfur release during black liquor combustion.

Kubelka and Voutopal[34] also reported reactions that could result in sulfur release from sodium sulfate:

$$Na_2SO_4 + CO \Rightarrow Na_2CO_3 + SO_2 \quad (26)$$

$$3Na_2SO_4 + CO_2 + Na_2S \Rightarrow 4Na_2CO_3 + 4SO_2. \quad (27)$$

The equilibrium constants of these reactions, however, make them unfavorable at most temperatures encountered in the boiler[34]. Also, the reactions mentioned above result in the production of SO_2. Since pyrolysis studies[16,17] report no sulfur dioxide being produced from kraft black liquor, it can be assumed that these reactions are not important contributors to the total

sulfur release.

Reactions of Organic Sulfur

The organic sulfur contained in kraft black liquor is assumed to be highly volatile under pyrolysis conditions[7]. Blackwell and King[33] state that it is likely that the organic sulfur reacts to form hydrogen sulfide; however, they neither cite any references nor report an assumed reaction mechanism.

Thermodynamics

Thermodynamic considerations have been used to explain some of the sulfur release behavior observed during black liquor combustion, particularly the decrease in the amount of sulfur volatilized at higher temperatures.

Strohbeen[5] calculated the equilibrium constants at several temperatures for the reaction

$$Na_2S + CO_2 + H_2O \Rightarrow Na_2CO_3 + H_2S \quad (3)$$

which is considered to be a major sulfur-releasing reaction. The results of these calculations indicate that, at temperatures of 300° C or less, complete volatilization of the sulfur as hydrogen sulfide is expected. The fraction of the sulfur being released to the gas phase decreases with increasing temperature until, at temperatures above 1000° C, all the sulfur should be present as sodium sulfide.

Others[26,38-40] have used thermodynamic considerations to predict the product composition present in a black liquor recovery boiler as a function of temperature, liquor composition, and combustion air. Bauer and Dorland[39] calculated the equilibrium constants at various temperatures for twenty reactions that were assumed to take place in a kraft recovery boiler during

black liquor combustion. Then, by making assumptions as to the quantities of reactants present during combustion, they were able to develop phase diagrams at the various temperatures. These diagrams plotted the concentrations of the various chemical species as a function of the log of the oxygen concentration. From the results of their calculations, Bauer and Dorland concluded that the optimum temperature for burning kraft black liquor is about 1400 K (1127^{o}C), noting that at lower temperatures the loss of sulfur to the gas phase is very high, while at higher temperatures the vaporization of sodium becomes excessive.

Rosen[40] considered the equilibrium compositions resulting from the burning of several different types of spent cooking liquors. He used the minimization of free energy to determine the products present at equilibrium. From his study of spent sulfate (kraft) liquor, Rosen concluded that some loss of sulfur and sodium to the gas phase was inevitable, that increasing the combustion temperature lowered the sulfur loss while raising the sodium loss, and the optimum operating condition for combustion of sulfate liquors was probably at a temperature of about 1400 K (1127^{o} C).

Borg et al.[26] calculated the sulfur and sodium emissions from a recovery boiler using a model that included field data and vertical and cross-sectional gradients in the furnace, as well as chemical equilibria in subsystems of the recovery furnace. They used this model to predict the amounts of sulfur and sodium volatilized during black liquor burning as a function of liquor solids, fraction of theoretical air, and temperature. The results of their model indicate that raising liquor solids reduces the amount of sulfur released, that sulfur release is a maximum at an air level of sixty to eighty per cent

of theoretical, and that increasing temperature decreases sulfur release up to temperatures of 2000° F (1093° C). At higher temperatures, sulfur release began to rise again.

Minimization of free energy was also used by Pejryd and Hupa[38] to determine the equilibrium compositions of various species in a recovery furnace during kraft black liquor combustion. They considered liquors with varying sulfur to sodium ratios and liquors with high amounts of impurities (potassium and chlorine), as well as theoretical "pure" liquors in their calculations.

For the theoretical liquor, the calculations indicated that the amount of H_2S decreased with increasing temperature in the range 600 - 1200°C, from about 10,000 ppm to about 200 ppm, although, at temperatures normally encountered in recovery boilers, the rate of decrease in hydrogen sulfide concentration with increasing temperature was small. COS emission was about one-tenth that of H_2S and followed the same trend. Emission of SO_2 became important only at high (>1000° C) temperatures. Increasing the sulfur to sodium ratio increased the amount of sulfur volatilized as H_2S and COS, almost an order of magnitude when the S/Na ratio is increased from 0.3 to 1.0. In addition, at very high sulfidities (S/Na = 1.0), the temperature dependence of hydrogen sulfide and carbonyl sulfide changes. For these liquors the amounts of sulfur present as H_2S and COS increases in the range 750 - 1000°C instead of decreasing as they do in lower sulfidity liquors. The presence of potassium and chlorine as impurities had little effect on sulfur's volatilization behavior.

Pejryd and Hupa[38] noted that the data of Borg et al.[26], which records gas

concentration measurements above a char bed, verify the predicted effect of temperature on H_2S concentration as a function of temperature. These data, shown in Table 7, are of the same order of magnitude as the predicted values and follow the trend of decreasing sulfur release with increasing temperature predicted by Pejryd and Hupa.

Table 7. H_2S emission from a char bed.[28]

Bed Temp. (°C)	H_2S Conc. (ppm)
720	5250
825	750
860	250

Analysis of Proposed Sulfur Release Reactions

The reaction mechanisms reported above support the idea that little or no sulfur will be volatilized from either sodium sulfate or sodium sulfite during black liquor pyrolysis[7]. The reported sulfate and sulfite reactions produce SO_2 as their volatile sulfur product. As pyrolysis studies have reported no sulfur dioxide being produced during black liquor pyrolysis, it may be assumed that the reactions of sulfate and sulfite mentioned above are not important in sulfur release during pyrolysis.

The proposed sodium sulfide reactions, on the other hand, show reduced sulfur gases, most notably H_2S, as the products formed during pyrolysis reactions. Pyrolysis studies[14,16,17] have shown that almost all the sulfur released from kraft black liquor is in the form of these reduced sulfur gases, with hydrogen sulfide dominating at higher temperatures. The most widely cited mechanism for H_2S production from sodium sulfide is reaction (3).

In contrast to the proposed sulfide reactions, which produce sulfur containing gases directly, most of the reactions cited above for thiosulfate produce either sodium sulfide or elemental sulfur which then undergoes additional reactions to produce sulfur-containing gases. Most of the proposed reactions for producing volatile sulfur species directly from thiosulfate show oxygen-containing sulfur species as a product. As these compounds are observed as minor components, if at all, during pyrolysis experiments[14,16,17], it is likely that most of the sulfur released by thiosulfate is first reacted to sulfide or elemental sulfur.

Thermodynamic considerations are usually employed to explain the observed decrease in sulfur release at high temperatures. This observation is confirmed by calculations that predict the complete product mix resulting from black liquor combustion in a recovery furnace[26,38-40], as well as simpler systems that consider only a single reaction[5].

MODELING OF SULFUR RELEASE DURING BLACK LIQUOR PYROLYSIS

Sulfur Release During Pyrolysis

Sulfur release during the combustion of kraft black liquor results in several serious problems in the recovery boiler. Much, if not all, of this sulfur is released during the pyrolysis stage of burning. Therefore, a model that will predict the amount of sulfur that will be released from a black liquor during pyrolysis would be an asset in efforts to minimize the amount of sulfur that is released in the recovery boiler. Such a model would describe the expected sulfur release as a function of liquor properties and the pyrolysis environment.

Pyrolysis Kinetic Models

Pyrolysis is often modeled as a first order decomposition reaction[41]. The amount of volatiles produced are usually assumed to be described by an Arrhenius-type equation of the form:

$$dV/dt = K_0 e^{-E/RT}(V^* - V) \qquad (28)$$

where:

V = Volatile yield at time t

t = Time

K_0 = Pre-exponential factor

E = Activation energy

R = Gas constant

T = Absolute Temperature

V^* = Maximum possible volatile yield.

Although these types of models are widely used to describe weight loss or volatiles evolution during pyrolysis of organic materials, they have often been found to be inadequate to accurately describe results of pyrolysis experiments that determine weight loss or complete volatile yield. One way to compensate for this inadequacy is to assume that the material being pyrolyzed volatilizes by two or more different reactions, each with its own activation energy and maximum yield[42]. An extension of this method is to postulate an infinite number of reactions, each with the same pre-exponential factor and gas yield, but with different activation energies. This approach results in a model having a distribution of activation energies, which, if assumed to be normal, can be characterized by a mean and standard deviation. Anthony[39] used this type of model to successfully describe the weight-loss behavior of coal

under pyrolysis conditions. A variation of this method divides the normal distribution into an arbitrary number of bands, each of which is assumed to represent a component of the pyrolysis material[42]. Other approaches include assuming the reaction to be other than first order[41], allowing the maximum volatile yield to be a function of temperature[43], or developing an entirely empirical predictive relation[41].

A more complex method of modeling pyrolysis is to monitor the production of the major gaseous species evolved during pyrolysis. These species are assumed to result from one or more first order reactions. Suuberg et al.[44] described coal pyrolysis by modeling eight major products. Each product was assumed to result from one to three independent, parallel reactions, each with a different pre-exponential factor, activation energy, and maximum yield. The overall results from such a model were found to be similar to models that employ a normal distribution of activation energies.

Analysis of Pyrolysis Kinetics Models

Since sulfur is released from black liquor as a result of pyrolysis reactions, modeling the volatilization of sulfur from kraft black liquor should be possible using the methods described above. The simplest of these methods is to describe sulfur release as resulting from a single, first-order, decomposition reaction. However, in view of the fact that sulfur release can result from more than one reaction and that the amount of sulfur volatilized decreases at higher temperatures, a more complex model may be necessary to successfully describe this phenomenon.

Heat Transfer Models

In order to model the sulfur release from a black liquor drop during pyrolysis, it is necessary to combine equations describing the volatilization of sulfur from black liquor as a function of time, temperature, and composition with expressions that describe the heating of the drop as a function of the drop's dimensions and composition and the heating environment in which the particle is being reacted.

Few models describing the heating of a black liquor drop during pyrolysis or burning have been developed. However, several models describing combustion and/or pyrolysis of other fuels are available. Of particular interest are models describing combustion of coal or coal-water slurries. Coal, when burned, goes through drying, pyrolysis/volatiles burning, and char combustion stages in a manner similar to black liquor[42]. Therefore, models that successfully predict the temperature of a coal particle or a coal-water slurry droplet during combustion may be applicable to black liquor combustion.

Frederick et al.[45] developed a model for the drying, devolatilization, and char burning stages of black liquor drops that were burned in two experimental reactors. It was assumed that drying and devolatilization were limited by external heat transfer, while char burning was assumed to be mass transfer limited. For each of the three stages, the elapsed time required for completion of the stage was calculated.

For drying, the elapsed time is the time required to transfer the heat required to dry the drop and is the upper limit of the integral in the

equation:

$$Q_{tot} = \int_0^{td} (dQ/dt)dt \qquad (29)$$

where:

Q_{tot} = total heat required for drying

dQ/dt = rate of heat transfer to the drop.

The heat required for drying was calculated to be the amount of heat required to heat the drop to the solids content at which the drop ignited plus the heat of vaporization of the water that was evaporated. The rate of heat transfer to the drop was calculated from the sum of the convective and radiative heat transfer terms.

The time required to complete devolatilization was similarly calculated from:

$$Q_{tot} = \int_0^{tv} (dQ/dt)dt \qquad (30)$$

where:

Q_{tot} = total heat required for devolatilization.

The heat required for devolatilization was the sum of the heat required to raise the temperature of the liquor solids to the maximum devolatilization temperature, the heat of devolatilization, and the heat required to evaporate any water that remained at ignition.

The time required for char burning was calculated as the upper limit of the equation:

$$M_{tot} = \int_0^{tc} (dM_c/dt)dt \qquad (31)$$

where:

M_{tot} = mass of carbon to be gasified

dM_c/dt = rate of char burning

The rate of char burning was calculated from the mass of carbon remaining to be gasified, the amount of oxygen required for char combustion, and the concentration of oxygen in the reactor.

The calculated times for each stage were compared to experimentally measured values. The experimental drying time was the time interval between when the black liquor drop entered the furnace and when the drop ignited. The experimental time for devolatilization was taken to be the time between the first appearance of a flame (drop ignition) and when the flame disappeared, or the time between ignition and maximum drop volume. Use of either criteria give nearly the same devolatilization time. The time for char burning was the amount of time that elapsed between the disappearance of the flame and the complete burnout of the drop's carbon. Good agreement between the calculated and experimental times for the stages could be obtained when appropriate values for the solids content at ignition and the carbon content of the char were selected.

Peck and Pollock[46] developed a model for the temperature history of a coal particle undergoing combustion in an aerodynamic levitation flow reactor. The energy equation describing particle temperature as a function of time was

$$m_p C_p dT/dt = Q_c + Q_r - h_{sg} dm_v/dt + \Delta h_v dm_v/dt + \Delta h_c dm_c/dt \qquad (32)$$

with:

m_p = particle mass

C_p = particle specific heat

T = particle temperature

t = time

Q_c = convective heat transfer

Q_r = radiative heat transfer

h_{sg} = enthalpy of sublimation

Δh_v = enthalpy of volatilization

Δh_c = enthalpy of carbon oxidation

m_v = mass of volatiles evolved

m_c = mass of char.

The rate of volatiles evolution was assumed to be first order with respect to the remaining volatile matter. An unreacted shrinking core model was used to determine char reaction rate. The rate was assumed to be first order with respect to oxygen concentration.

The model's results were compared to experimental values of temperature measurements made on 2-6 mm diameter pelletized coal spheres that were burned in the aerodynamic levitation flow reactor. The calculated time/temperature profiles had the same shape and, in the early stages of burning, similar values to temperature profiles measured with an infrared pyrometer.

Sandhu and Hashemi[47] developed a model for a coal particle being heated by convection and radiation in an inert gas stream. It was assumed that the temperature inside the coal particle was uniform and that the particle did not swell. The particle temperature as a function of time was described by

$$dT/dt = (q_c + q_r)\pi d_a^2/mC_p - (-dm/dt)\Delta H_d/mC_p \qquad (33)$$

with:

T = temperature of the particle

t = time

q_c = conduction heat transfer

q_r = radiation heat transfer

d_a = particle diameter

m = particle mass

C_p = specific heat of coal

ΔH_d= enthalpy of coal devolatilization

The rate of mass loss, dm/dt was calculated by assuming that the decrease of mass was described by a first order reaction.

The model was used to predict the temperature and mass loss as a function of time for 50 to 100 μm diameter coal particles. No comparisons of the model with experimental results were reported.

Murdoch et al.[48] modeled the combustion of a coal-water slurry drop in a furnace. The drop was assumed to be spherical and to receive heat from the furnace walls and from the surrounding air or flame. The coal was assumed not to swell during combustion. The temperature of the surface of such a drop was given by

$$dT_s/dt = [(Q_c + Q_r + Q_s + Q_{ox}) - L_w dm_w/dt]/\beta(t) \qquad (34)$$

with:

T_s = surface temperature

t = time

Q_c = conductive heat flux from air to surface

Q_r = radiative heat flux

Q_s = conductive heat flux from surface to particle interior

Q_{ox} = heat evolved by char combustion

L_w = latent heat of water

dm_w/dt= rate of evaporation

$\beta(t)$ = mass of surface times specific heat of surface

The model was tested against measurements of burning drops whose temperatures were measured using two-color pyrometry. For a 1.3 mm diameter drop, the model was found to give good agreement with experimental data during the early (drying and pyrolysis) stages of combustion, and fair agreement for the later (char burning) stages.

Analysis of Pyrolysis/Combustion Models

The models described above have shown the ability to calculate the temperatures obtained by fuel particles during pyrolysis and/or burning. The agreement between the calculated and predicted temperatures or times is usually best for the early (drying and pyrolysis/volatiles burning) stages. The models assume that drying and devolatilization are external heat transfer limited. Therefore, a model describing heat transfer to and through a pyrolyzing black liquor drop should be able to describe the temperatures obtained by the drop. Problems that will have to be addressed with the proposed black liquor model include the calculation of temperature gradients within the particle and the changes in drop density and volume due to swelling.

OBJECTIVES

A fundamental understanding of the phenomenon of sulfur release during the pyrolysis of kraft black liquor does not exist. It is known that the different sulfur species that are present in black liquor behave differently under pyrolysis conditions, but specific data on the release of gaseous sulfur as a function of time and temperature are not available, and some of the results previously obtained are contradictory. In addition, the influence that changing a black liquor drop's physical characteristics, such as particle size, solids content, and degree of swelling have on the release of sulfur has not been determined.

This study examined sulfur release during the pyrolysis of kraft black liquor by quantifying and modeling the effects of important compositional and physical variables on the release of sulfur. Specifically, the objectives of this thesis were:

1. To quantitatively determine the amounts of sulfur volatilized from sodium sulfate, sodium sulfite, sodium thiosulfate, sodium sulfide, and organic sulfur as a function of time and temperature during pyrolysis of black liquor drops.
2. To determine the effect of changing the particle size, solids content, and degree of swelling on the amount of sulfur released from a black liquor drop.
3. To report these findings in a model that will describe the volatilization of sulfur during pyrolysis of a drop of kraft black liquor.
4. To recommend appropriate ways to minimize sulfur release from burning

black liquor drops within a recovery furnace.

EXPERIMENTAL APPROACH

The first part of the thesis concentrated on determining the volatilization characteristics of the various sulfur compounds present in black liquor. Kraft black liquor contains several different sulfur species and it was expected that these different compounds would behave differently with respect to sulfur release during pyrolysis. In order to measure the effect of each sulfur species separately, it was necessary to prepare black liquors containing only a single sulfur species. These liquors were then pyrolyzed and the contributions of each sulfur species to the total sulfur release determined.

It was desired to determine a kinetic expression describing the behavior of each sulfur species as it undergoes pyrolysis. By varying the reaction time and the temperature to which the sulfur species was exposed and measuring the amount of sulfur gas produced, data was obtained that allowed generation of a kinetic model describing sulfur volatilization from the various sulfur species.

During the second part of the experimental work, the effects that varying the black liquor particle's physical characteristics have on the amount of sulfur release were determined. Because it was suspected that temperature gradients within a black liquor particle might influence the amount of sulfur that is volatilized, the transfer of heat through the black liquor drop itself was determined, as well as heat transfer to the drop. To determine the heat transferred through the particle, it was necessary to measure both the external and internal temperatures of the pyrolyzing particle. The variables that were anticipated to be important in determining the heat transfer behavior of black

liquor drops and that had been identified as influencing sulfur release were particle size and solids content.

One factor that had not been considered in sulfur release studies is what effect the degree to which the drop swells during pyrolysis affects the drop's sulfur release behavior. Liquors resulting from the pulping of highly resinous species[49] or to which extractives have been added[13] swell less during combustion than do extractive free liquors. These low swelling liquors have been found to produce chars that have higher activation energies than do chars produced from high swelling liquor. The chars resulting from low swelling liquors burn longer and colder than do the chars resulting from liquor that exhibits high swelling[49,50]. It was believed that a liquor's swelling characteristics would influence its sulfur release behavior during pyrolysis as swelling would affect particle size and density and, therefore, the rate of heat transfer to and through the drop. Because of these considerations, the effect of swelling on sulfur release was also investigated as part of the heat transfer studies.

After the chemical composition and physical variables data were gathered, a model predicting the amount of sulfur being volatilized from a black liquor drop during pyrolysis was written. This model was similar in form to the models for coal mentioned above. In these models the temperature of the particle is described as a function of time and the conditions under which the coal particle is being pyrolyzed or combusted. This temperature was then used in kinetic expressions to predict the amount of sulfur released.

Finally, this model and the results of previous studies on the release of

sulfur during black liquor burning were used to draw conclusions on the factors that influence sulfur release during black liquor combustion in a recovery boiler and to recommend steps that could be taken that would minimize the release of sulfur during black liquor combustion.

EXPERIMENTAL

MATERIALS

The amount of sulfur volatilized from a particular sulfur species depends on the organic material with which the sulfur is pyrolyzed[30,31]. Therefore, for the experiments designed to determine the kinetics of sulfur release, it was desirable to use a substrate whose organic composition is similar to that found in kraft black liquor. It was also necessary to be able to control the amounts and species of the sulfur contained in the liquor. For these reasons, a soda black liquor was chosen for use as the organic substrate in the experiments to determine sulfur release kinetics.

In soda pulping the active chemical species is sodium hydroxide. Kraft pulping, on the other hand, uses both sodium hydroxide and sodium sulfide to remove lignin from the wood. Both pulping processes are alkaline and both remove lignin by breaking the lignin's alkyl-aryl ether bonds to form fragments that are soluble in the pulping liquor. In kraft pulping, this process is accelerated by the sulfide ion, which not only breaks alkyl-aryl ether bonds in a sulfidation reaction, but also reacts with groups in lignin that would otherwise condense. The cellulose fraction of the wood is relatively stable in both pulping processes[51]. Thus, a soda black liquor should contain dissolved wood components similar to those found in kraft black liquor.

For the heat transfer experiments, where it was not necessary for the sulfur to be present as a single species, a kraft liquor was used. It was desirable that this liquor have a chemical composition similar to that of typical mill kraft liquors.

The soda and kraft black liquors were produced in laboratory scale cooks. The cooking conditions and pulp and liquor characteristics are shown in Table 8. Sodium carbonate and sodium sulfate were added to the kraft cooking liquor so that this liquor would simulate the composition of mill liquors, which contain significant amounts of these compounds.

Table 8. Cooking conditions and results of laboratory cooks.

	Soda Cook	Kraft Cook
Effective Alkali (% on OD wood as Na_2O)	22	16
Sulfidity (% of active alkali)	0	25
Liquor/Wood Ratio	4	4
Cooking Temperature (^oC)	173	173
Time to Temperature (min)	90	90
Time at Temperature (min)	172	94
Dead Load Chemicals (based on OD wood as % Na_2O)		
Na_2SO_4	0.0	0.571
Na_2CO_3	0.0	3.430
Kappa Number	36.3	26.4
Yield (%)	41.3	46.5
Liquor Solids (%)	16.2	16.6
Liquor NaOH Concentration (as %Na_2O)	9.5	7.8

The soda and kraft liquors were concentrated in a rotary vacuum distillation apparatus at 50 mm of vacuum and temperatures less than 100^o C to twenty-five to thirty per cent solids. The liquors were then filtered through a fine mesh screen to remove any soap that had formed during concentration. Rotary vacuum concentration was then continued until the liquors were concentrated to fifty per cent solids. The liquors were then analyzed for elemental composition. The results of these analyses, shown in Table 9, indicate that both liquors have similar elemental compositions (except for sulfur).

Table 9. Elemental compositions of soda and kraft liquors.[a]
Per Cent of Total Solids

Element	Soda	Kraft
Carbon	40.7	37.6
Hydrogen	4.0	4.1
Oxygen	33.8	34.2
Sulfur	0.0	2.8
Potassium	0.6	0.6
Sodium	20.4	20.9

[a] Analysis by Huffman Laboratories, Golden, Colorado

To prepare liquors containing only a single sulfur species, solutions of sodium salts of the various sulfur species which were to be tested for sulfur release kinetics were added to samples of the soda liquor. The sulfur species added were sulfate, sulfite, thiosulfate, and sulfide. The sulfur species were added in quantities designed to produce liquors containing 3.5% sulfur, except for the sulfide, which was added in a quantity designed to produce a liquor that was 3.0% sulfur. The liquors were then reconcentrated by rotary vacuum distillation under the same conditions as before to approximately sixty-five per cent solids. After their preparation, the liquors were analyzed for sulfur content.

The liquors' sulfide concentration was determined by potentiometric titration with a specific ion electrode. The method used is the same method as found in TAPPI method T625 cm-85[52] with the exception that a mercury-mercuric sulfide electrode and mercuric chloride are used as the electrode and titrant respectively, instead of the silver-silver sulfide electrode and silver nitrate titrant specified in the TAPPI standard. The black liquor sample is diluted with water and NaOH and an anti-oxidant are added. The titrant is then added in small increments and the resulting Emf monitored.

When addition of the titrant results in a large drop in Emf, two additional increments of titrant are added and the titration is ended. The concentration of sulfide is determined by plotting the volume of titrant used vs Emf and reading the volume at the inflection point of the resulting S-shaped curve.

The sulfate, sulfite, and thiosulfate concentrations were determined by ion chromatography (IC) using TAPPI method T699 om-87[53]. In this procedure, a dilute sample of black liquor is injected into an ion chromatograph. The peaks resulting from sulfate, sulfite, and thiosulfate are identified by comparing the chromatogram obtained from the black liquor sample to chromatograms of standard solutions. The concentrations of sulfate, sulfite, and thiosulfate are determined by measuring their peak areas and comparing them to peak areas obtained from the standard solutions. The repeatability for IC determination of sulfur species concentration in black liquor is twelve per cent (of the mean value) for sulfate, sixteen per cent for thiosulfate, and thirty per cent for sulfite. These values of repeatability are the maximum expected difference between two test results, each of which is based on a single determination[53].

Results from this method of determining the concentrations of the oxidized sulfur species have been compared with results obtained from other methods of sulfur analysis. Sulfate determination by IC has been found to give good agreement with sulfate determinations determined by titration with lead perchlorate using a specific ion electrode. Both the IC and titration method give results that are somewhat lower than the more traditional method of measuring sulfate content by precipitation with barium chloride[54]. Koivuniemi et al.[54] state that the difference in results can be attributed to oxidation

of other black liquor sulfur compounds to sulfate during the acid pretreatment used in the precipitation method, and that the IC and titration methods are preferred as they give a direct measurement of the sulfate content. Thiosulfate measurements made by ion chromatography have been compared to measurements made by titration using a specific ion electrode and have been found to give good agreement[55].

The total sulfur content was determined in a separate test which involved combustion of the liquor in an oxygen-filled Schoniger flask to convert all the sulfur to sulfate, followed by ion chromatography to determine the resulting sulfate concentration. This method for determining sulfur content has been compared to total sulfur measurements made by two other methods: 1. oxidation of the sulfur to sulfate with hydrogen peroxide followed by ion chromatography, and; 2. digestion of the liquor with nitric and perchloric acid to convert the sulfur to sulfate followed by precipitation of the sulfate with barium chloride.[56] All three methods were found to give similar (within 5%) results.

Some of the total sulfur measurements were made by Huffman Laboratories, Golden, Colorado using ASTM method D4239-85[57]. This test method, which was developed for measuring sulfur content in coal, combusts the sample in a high temperature (1350^{o} C) furnace and measures the concentration of SO_2 and SO_3 produced.

An exception to this procedure was made for the liquor to which sodium sulfite had been added. For this liquor, the results of the sulfite content determinations as measured by IC varied widely and did not agree with the

amount of sulfur found by the total sulfur test. Therefore, the sulfite concentration was determined by a modified Palmrose Iodate titration[58]. This test method is a modification of a method used to measure the strength of acid sulfite pulping liquors[59], and is similar to other titration methods that have been used to measure sulfite concentration[5].

In the modified Palmrose Iodate test, the black liquor sample is dissolved in water. If sulfides are present in the liquor, they are removed by mixing the black liquor sample with a zinc carbonate suspension. The liquor is then filtered and a sample of the filtrate is acidified with sulfuric acid. Postassium iodide is added and the sample is titrated with potassium iodate using a starch indicator. The results of this titration indicate the amount of sulfur present as sulfite and thiosulfate. For the sulfite-containing liquor, the amount of thiosulfate found by IC was subtracted from the results of the titration, giving the concentration of sulfite.

The results of the analyses are shown in Table 10. These results indicate that, although most of the sulfur found in the liquor was in the form in which it was added, some conversion to other sulfur species had taken place during the liquor preparation. The column labeled "Sum of/Col. 1-4" gives the sum of the four inorganic sulfur species tested; the "Total/(Test)" column reports the results of the separate total sulfur test.

When black liquor containing sodium sulfide is exposed to air, there is the possibility that the sulfide will oxidize to thiosulfate. Therefore, for the liquor containing sodium sulfide, precautions were taken to mimimize the

Table 10. Sulfur analysis of soda liquors with added sulfur.
All Values as Per Cent Sulfur

Species Added	Content Reported as SO_4^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S^{2-}	Sum of Col. 1-4	Total (Test)
Sulfate	2.80	0.00	0.00	0.00	2.80	2.96
Sulfite	0.24	2.24	0.37	0.00	2.85	3.07
Thiosulfate	0.12	0.00	3.00	0.03	3.15	3.27
Sulfide[a]	0.07	0.32	0.97	1.70	3.06	2.88[b]

[a] Analysis done after completion of pyrolysis tests
[b] Analysis by Huffman Laboratories, Golden, Colorado

oxidation of the sulfide during the pyrolysis tests. The liquor sample was stored in a cold room under nitrogen between sets of tests. While the tests were being conducted, the bottle containing the liquor was kept covered except when liquor samples were being extracted. Also, the sample bottle was purged with nitrogen several times during the course of a test set. The liquor was checked for sulfide content just after the liquor was formulated and several times during the course of the experimental runs. The liquor was also checked for thiosulfate content immediately after formulation and at the end of the experimental tests. The sulfide content was determined by titration with silver nitrate using a specific ion electrode; the thiosulfate by a modified Palmrose-iodate titration. The sulfur content immediately after formulation was 2.18% sulfur as sulfide; 0.40% as thiosulfate. The average of seven sulfide content measurements made during the course of the pyrolysis runs was 2.09 ± 0.13%. The thiosulfate content measured after completion of the pyrolysis runs was 0.49%. Therefore, for all sulfide tests, it was assumed that the liquor contained 2.09% sulfur as sulfide and 0.49% as thiosulfate.

A liquor that contained only organic sulfur was also needed. To obtain such a liquor, it was necessary to remove the ionic sulfur species from the kraft liquor. The method used to accomplish this removal is described in Appendix 1. This liquor was also analyzed for sulfur content. The results of this analysis showed a sulfate content (as % sulfur) of 0.10%, a sulfite content of 0.16%, and a total sulfur content of 0.58%.

APPARATUS AND PROCEDURE

Pyrolysis Kinetics Experiments

The pyrolysis kinetics experiments were conducted in a captive sample reactor (Fig. 1). Similar reactors have been used to study pyrolysis of coal[41] and kraft lignin[43]. The reactor body was constructed of polyvinyl chloride and consisted of a gas expansion chamber, a stage to hold the electrodes in place, and a removable Pyrex dome. The dome allowed visual observation of the pyrolysis reaction. The black liquor sample (equivalent to approximately seven milligrams of solids) was held within a folded strip of 250 mesh stainless steel wire that was clamped between two semicircular brass clamps (three-fourths inch radius). The clamps are soldered to electrodes made of one-inch diameter brass rod. This apparatus allows the black liquor to be pyrolyzed as a very thin film. The small film thickness, along with the fact that heat is applied to both sides of the black liquor film by the folded wire screen, insures that the black liquor sample is heated to the screen temperature almost instantly.

The sample was heated by electrical resistance. Two parallel heating circuits were employed, one to heat the sample to the desired temperature, the

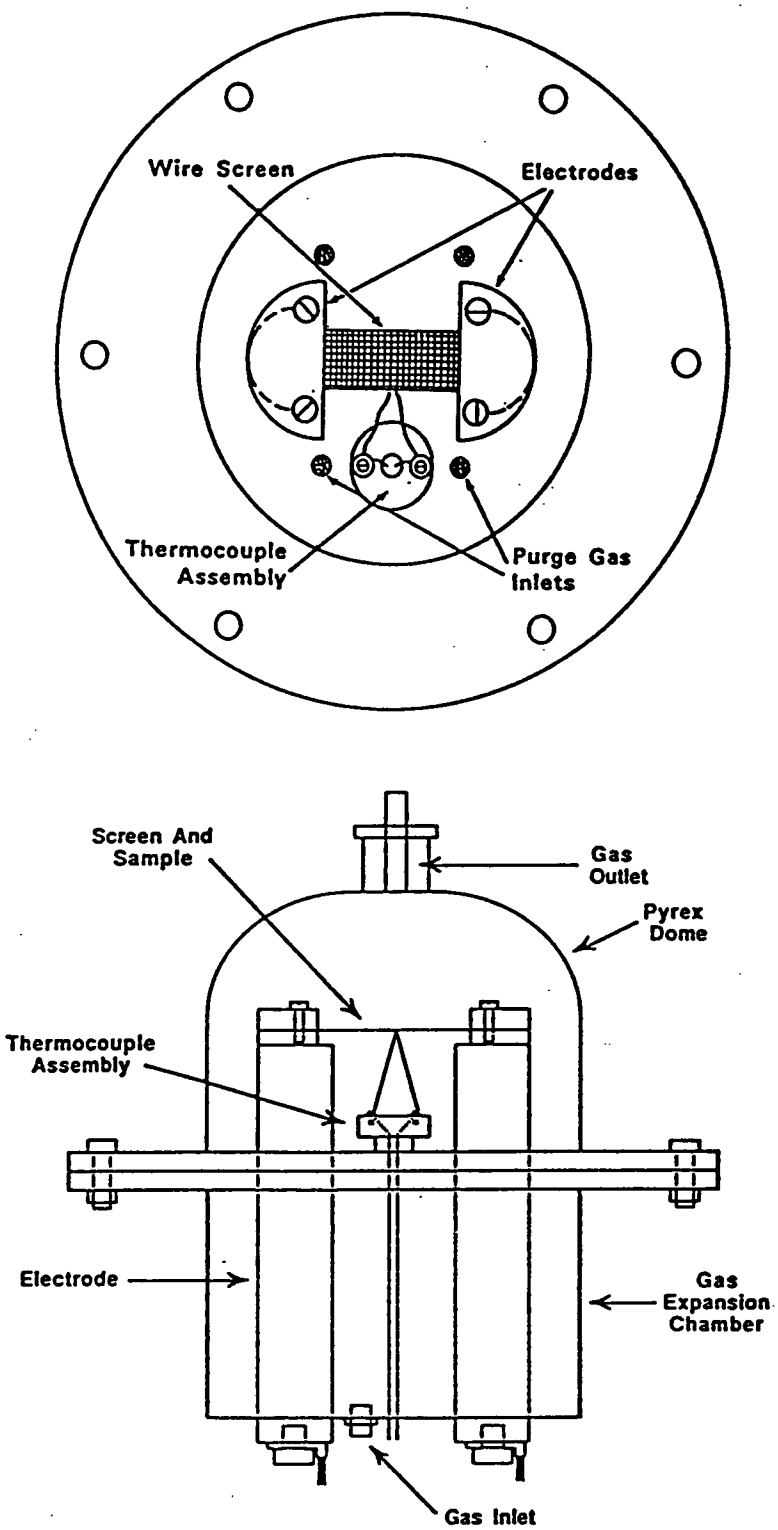

Fig. 1. Pyrolysis kinetics reactor - top and side view.

other to maintain the temperature at the desired level. Electrical power was supplied by 115 V household current. The current was fed to two variable auto transformers (Superior Electric Powerstat Type 116) which provided a variable voltage of up to 140 volts at a maximum of 7.5 amps. The current from the transformers was fed to a timer/controller circuit consisting of a toggle switch and two timers (Syracuse Electronics model TVR 003**). The first of these, a zero to one second timer, was connected to the first of the two transformers, which was set at full power, and was activated when the switch was engaged. Varying the timer's setting allowed the circuit to heat the liquor to the desired temperature. The second timer, which was engaged immediately upon completion of the first timer's interval, was connected to the second transformer and provided power to maintain the sample at the desired temperature. The constant temperature level was controlled by choosing the correct voltage setting on the variable transformer. This timer can maintain the temperature for as long as fifteen seconds. The current from the timers was fed to four transformers (Kenyon type S-13377 20:1) that were aligned in series. These transformers supplied current to the brass electrodes. The heating system allowed heating rates of up to four thousand degrees C per second (heat flux of 500 kW/m^2) and could pyrolyze liquor samples at temperatures of one thousand degrees or more.

The temperature of the sample during the pyrolysis run was measured by a thermocouple (Omega, Chromel-Alumel bare wire .003" diameter) that was folded into the wire with the sample. The thermocouples used have an error of five degrees C or less over the range of temperatures used in the pyrolysis tests[60]. The signal from the thermocouple was monitored using a strip chart

recorder.

During a pyrolysis run the black liquor sample was applied to one side of the wire screen which was then folded over onto the sample and clamped between the electrodes. The thermocouple was inserted into the fold and the dome bolted into place. The reactor was purged with nitrogen for several minutes. The heating circuits were then engaged. The gases produced by the pyrolysis were swept by the nitrogen out of an opening in the top of the dome and carried through a length of heat-traced Teflon tubing to a 1.9 cm quartz combustion tube. There the gases were mixed with air and burned in the combustion tube which was located inside a tube furnace. The furnace was heated to 900 degrees C. This burning converted the reduced sulfur gases produced during pyrolysis to SO_2. From the combustion tube, the gases were transported through another length of heat traced Teflon tubing to an SO_2 meter (Teledyne Series 600 Photometric Analyzer). The meter measures sulfur dioxide concentration by absorption of ultraviolet light. The wavelength employed, 289 nanometers, is used because SO_2 absorbs at this wavelength with little or no interference from other pyrolysis products. The signal from the sulfur dioxide meter was recorded on a strip-chart recorder. The amount of sulfur released was determined by measuring the area under the absorption curve recorded on the strip chart using a graphics tablet attached to a computer (Apple II Plus). This method of determining the amount of sulfur released, rather than measuring the amount of the individual sulfur species, was used as the combustion/SO_2 analysis procedure is much simpler than isolating each indiviual gaseous sulfur species and measuring its concentration. Also, in properly operating recovery boilers, all of the

reduced sulfur species are oxidized to SO_2 or captured by fume prior to their release from the boiler. Therefore, only the total amount of sulfur released is of practical importance. The entire reactor system is shown in Fig. 2.

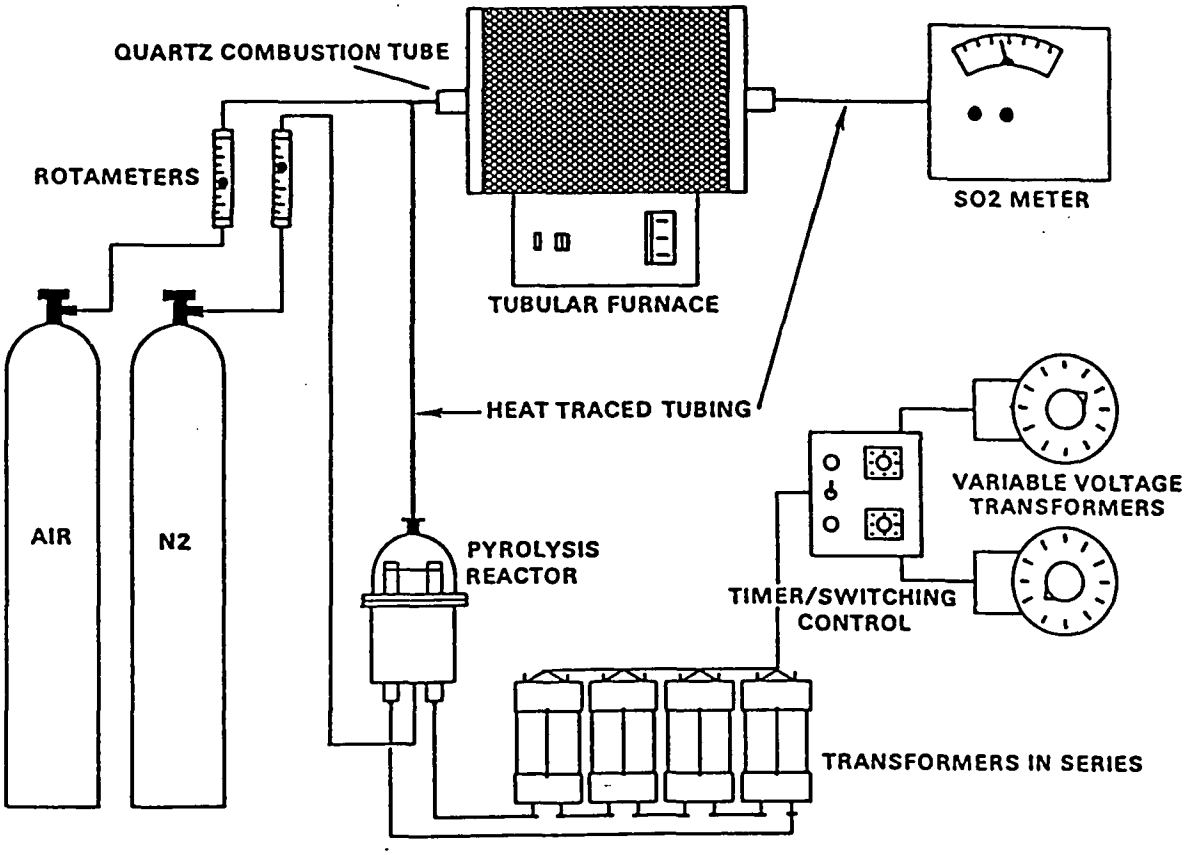

Fig. 2. Pyrolysis kinetics reactor system.

Tests were conducted to insure the reactor system's ability to accurately measure the amount of sulfur-containing gas released during liquor pyrolysis. A gas containing 49.7 ppm H_2S, 46.8 ppm CH_3SH, and 49.4 ppm COS was passed through the reactor system and the SO_2 concentration resulting from the gas's

combustion in the heated combustion tube measured. The results of these tests showed that 94 to 96% of the sulfur contained in the test gas was detected as SO_2.

Several additional tests were performed to characterize the reactor system. These tests were done: 1. to insure the wire screen heated the liquor uniformly, 2. to determine if there was significant reaction between the screen and the releasing sulfur gases, and 3. to test the effect that changing the heating rate had on the amount of sulfur released from the black liquor. The details and results of these tests are shown in Appendix 7. The results of the tests indicated that: 1. the temperature of the screen was reasonably uniform during the pyrolysis tests, 2. no significant reaction between the wire screen and the releasing sulfur gases was detected, and 3. changing the heating rate from 3972^{o} C/sec to 2305^{o} C/sec did not affect the amount of sulfur released during pyrolysis.

Heat Transfer Experiments

Heat transfer experiments were conducted using the convective single particle reactor (SPR). The reactor, pictured in Fig. 3, has a movable lower section that allows the insertion of black liquor drops. Heat for pyrolyzing or burning the particle is supplied by a gas stream which, by means of a baffle, can be directed onto the drop or through a bypass channel. Additional heat may be supplied by a radiant heater located in the sample area. Air, nitrogen, or a mixture of the two can be supplied as the combustion or pyrolysis gas. A view port allows visual or photographic observation of the pyrolysis process. The particle may be attached to a microbalance which allows continuous monitoring of the particle's mass.

Neither the radiant heater nor the microbalance were used in the heat transfer experiments described below.

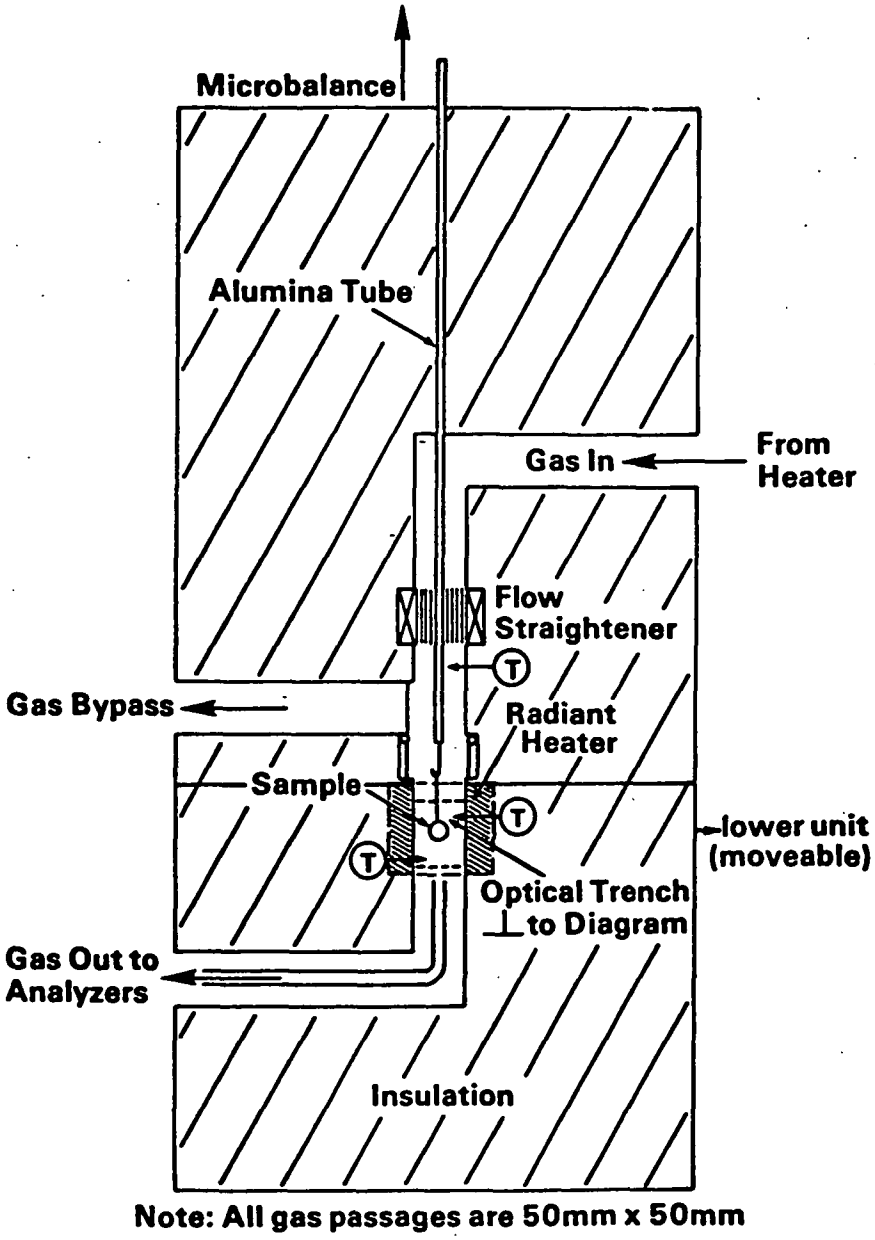

Fig. 3. Convective single particle reactor.

The liquor used for the heat transfer experiments was the kraft black liquor that was generated by the lab cook. The liquor was evaporated using vacuum distillation to produce liquors of varying solids levels for testing. Liquors having solids contents of 62.7%, 66.9%, and 74.0% were produced.

In order to determine the effect of liquor swelling on heat transfer to and through a black liquor drop, it was necessary to modify the swelling behavior of the liquor. The addition of extractives tends to suppress black liquor swelling during pyrolysis[13]. The swelling retardant chosen for these experiments was pine rosin, which was added to a sample of the 74.0% solids liquor. The rosin, equivalent to seven per cent of the liquor's solids content, was dissolved in a small amount of sodium hydroxide and mixed with the liquor. The solids content of this liquor was then rechecked to insure that no significant change in solids content had occurred as a result of rosin addition.

After the liquors were prepared, their swelling characteristics were measured. Drops of each liquor were formed on a nichrome wire, weighed on an analytical balance, and inserted into the single particle reactor under nitrogen flow at a nominal gas temperature of 800^{o} C. The drops were allowed to swell and were photographed. A one-half inch steel ball was also photographed for use as a standard. The negatives obtained from these photographs were placed in a photographic enlarger and the outlines of the drops traced on paper. The projected areas of the drops and the reference standard were determined using the graphics tablet. The volume of each drop was calculated by assuming that the drop was spherical and had a projected area equal to the area measured. This technique has been used previously in

studies of black liquor swelling with good results[13].

To measure the heat transferred to and through a pyrolyzing black liquor particle, measurements of both surface and internal temperature were needed. These temperatures were obtained by use of an optical pyrometer (Wahl model HSM-674) and a thermocouple, respectively.

Various size drops of the four liquors were formed around the bead of a bare-wire thermocouple (Type K - .006" diameter wires). Because weighing the thermocouple/droplet assembly to obtain a measure of particle size was impractical, the particles were photographed and the drop's volume determined in the same manner as described above. The mass was then calculated using the liquor's solids content and Cantrell's[22] equation for determining liquor density:

$$\rho = 4.072\ E\text{-}06 * W^2 + 4.137\ E\text{-}03 * W + 1.0 \qquad 35)$$

where:

ρ = Liquor Density (g/cc)

W = Liquor Solids (%).

This equation was developed by measuring the displacement of decane using samples of various solids of a black liquor similar to that used in this study.

After the drops were photographed, they were inserted into the reactor, the SPR was closed, and the optical pyrometer focused on the drop. The particles were pyrolyzed using nitrogen (100 slpm, 800^{o} C nominal temperature). The signal from the pyrometer and the thermocouple were collected at 0.436 second intervals by an ISAAC data collection system (Cyborg

model 41A) and stored on floppy disks by a computer (Apple II Plus).

Determination of Size, Solids, and Swelling Effects

To determine the effects of particle size, solids content, and degree of swelling on the amount of sulfur released during black liquor pyrolysis, drops of various sizes, solids content, and swelling characteristics were pyrolyzed in the radiant single particle reactor. This reactor is pictured in Fig. 4. This reactor, rather than the convective single particle reactor was used because the large gas volumes used in the convective single particle reactor and the potential for air leaking into the reactor made gas sampling and analysis difficult. The radiant single particle reactor consists of a mullite tube that is partially filled with ceramic packing. Heat is supplied to the tube by electrical heaters that surround the reactor body. Air, nitrogen, or a combination of the two is introduced at the bottom of the tube. In the experiments described below only nitrogen was introduced into the reactor. The temperature of the gas in the reactor is monitored by a thermocouple. For this set of tests, the gas temperature was controlled to 665^{o} C. The liquor sample is formed into a drop around a nichrome wire and is introduced into the reactor by attaching the wire to the sample rod/plug which is then inserted into the reactor through an access hole in the reactor cover. The gases produced by the drop's reactions are carried out of the reactor by the purge gas through an opening in the reactor cover. The gaseous products are then mixed with air, burned, and analyzed for sulfur content in the same manner as with the pyrolysis kinetics experiments.

The liquors used to determine the effect of particle size, solids content, and degree of swelling on sulfur release were the same liquors used

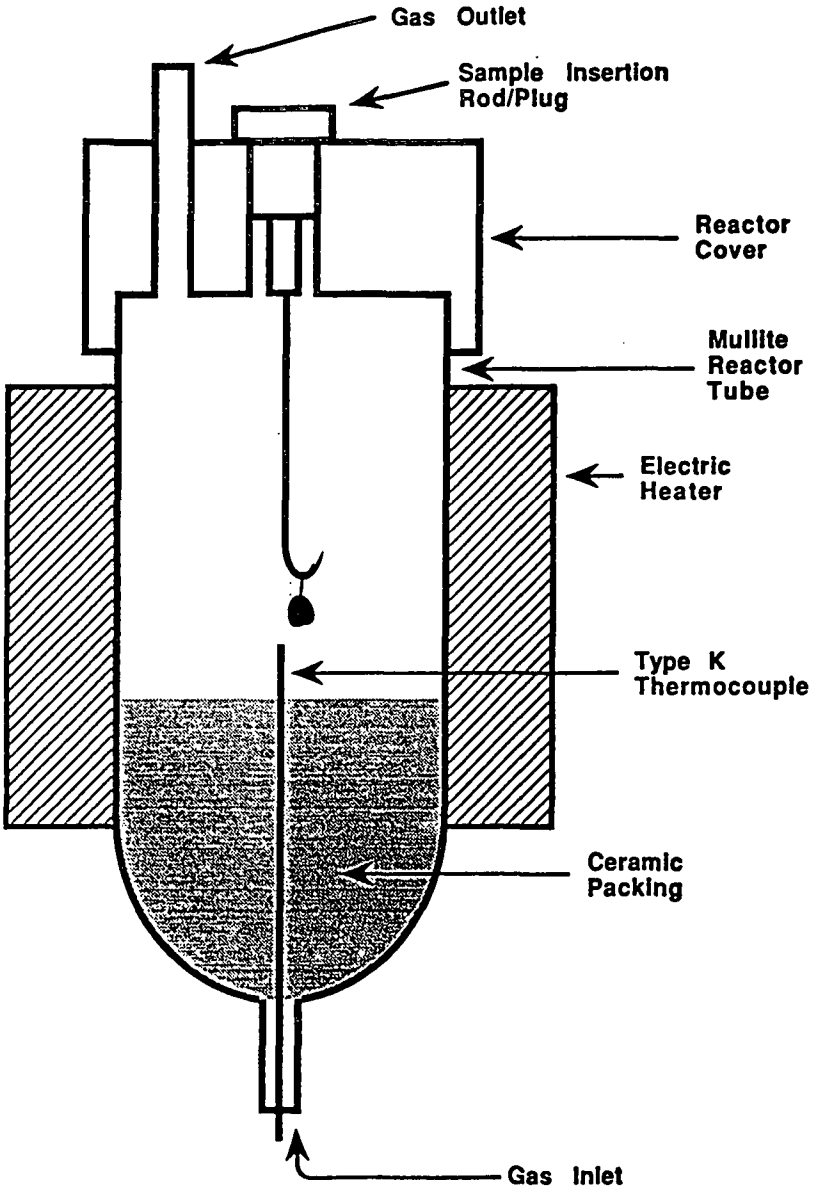

Fig. 4. Radiative single particle reactor.

to measure the heat transfer characteristics. The liquors having the lowest solids, highest solids, and the liquor to which the swelling retardant had been added were used. Because of evaporation during the course of performing

the heat transfer experiments, the liquors' solids contents had increased slightly. The new solids contents of the liquors tested were: low solids liquor - 63.4%; high solids liquor - 77.8%; liquor with swelling retardant added - 76.7%. For each liquor, three different drop sizes were tested. Seven replicates were run at each treatment combination.

RESULTS AND DISCUSSION

PYROLYSIS OF SODIUM SULFATE

The results of the pyrolysis experiments performed on soda black liquor that had been mixed with sodium sulfate are summarized in Table 11. In this and in subsequent tables, the column labeled "Time at Temp." refers to the time that the sample was held at the nominal pyrolysis temperature only, and does not include any heating or cooling time. It is recognized that the heating and cooling times will differ for pyrolysis tests made at different temperatures and that sulfur is released during these times as well as when the liquor is at the nominal pyrolysis temperature. These factors and the method used to account for them are discussed below in the section entitled "SULFUR RELEASE MODEL". The tests are grouped according to runs that employed the same pyrolysis time and a similar pyrolysis temperature during the constant temperature portion of the test. The 95% confidence limits shown were determined from the sample variances calculated for each test group. For tables in which only a single confidence limit is listed, the variances of the different test groups have been found not to differ significantly (as determined by Bartlett's Test[61]) and a "pooled" variance has been used in determining the confidence limits. The column labeled "Ave. Temp." reports the average of these constant temperatures for each group. The individual test results are shown in Appendix 2. The column titled "Sulfur Released/(per cent)" refers to the per cent of the liquor's major sulfur species (in this case, sulfate) sulfur that has been released. With the exception of pyrolysis runs performed on sulfide-containing liquor, it has been assumed that all released sulfur comes from the major sulfur species. The results of the

individual tests are given in Table 23 in Appendix 2.

Table 11. Pyrolysis of sulfate-containing soda liquor.
64.0% solids liquor; 6.1 - 7.7 mg solids sample size

No. of Tests	Time at Temp. (sec)	Ave. Temp. (°C)	Sulfur Released (mg S/100 g solids) (± 95% C.L.)	(per cent)[a] (± 95% C.L.)
10	4.5	443	3 ± 4	0.11 ± 0.14
10		749	10 ± 5	0.36 ± 0.18
10	10.5	448	5 ± 5	0.18 ± 0.18
10		742	16 ± 8	0.57 ± 0.29
10	15.0	452	8 ± 8	0.29 ± 0.29
10		745	30 ± 14	1.07 ± 0.50

[a] Initial sulfate content based on Table 10

The results of the sodium sulfate pyrolysis tests show that very little sulfur is released from sulfate during pyrolysis. These results are similar to results of pyrolysis studies of sodium sulfate with model compounds reported by Douglas and Price[30] and Strohbeen and Grace[31] which indicated little or no release of sulfur during sodium sulfate pyrolysis.

PYROLYSIS OF SODIUM SULFITE

Table 12 summarizes the results of pyrolysis experiments that were performed on sodium sulfite-containing soda liquor. The results of the individual tests are shown in Table 24, Appendix 2. While the amounts of sulfur released during sulfite pyrolysis are larger than those volatilized from sodium sulfate, the amount of sulfur released is still quite small. The results obtained in this study are similar to those obtained by Douglas and Price[30] and by Strohbeen and Grace[31]. The amounts of released sulfur observed by Strohbeen and Grace for pyrolysis of sulfite with vanillic acid are somewhat higher than

those of the present study; however, Strohbeen[5] suggests that acidic stripping of the sulfite by the vanillic acid may be responsible for these results.

Table 12. Pyrolysis of sulfite-containing soda liquor.
66.1% solids liquor; 6.1 - 7.5 mg solids sample size

No. of Tests	Time at Temp. (sec)	Ave. Temp. (°C)	Sulfur Released (mg S/100 g solids) (± 95% C.L.)	(per cent)[a] (± 95% C.L.)
10	4.5	441	44 ± 8	1.96 ± 0.34
10		709	32	1.43
10	10.5	442	36	1.61
10		707	39	1.74
10	15.0	446	57	2.54
10		710	45	2.01

[a] Initial sulfite content based on Table 10

The amount of volatilized sulfur shown in Table 12, while small, may actually overestimate the amount of sulfur released from sodium sulfite during pyrolysis. The liquor used contained minor amounts of thiosulfate (about 10% of total, see Table 10). This thiosulfate probably resulted from reaction by the sulfite in solution during liquor preparation. The sulfur contained in thiosulfate is quite volatile under pyrolysis conditions and the sulfur gases observed could be due totally or in part to volatilization of the sulfur present as thiosulfate.

PYROLYSIS OF SODIUM THIOSULFATE

Table 13 gives a summary of the results obtained from pyrolysis experiments using the soda liquor which contained sodium thiosulfate. The individual test results can be found in Table 25, Appendix 2. The results

summarized in Table 13 show that the amount of sulfur released during pyrolysis of the liquor increases with increasing temperature until a level of 450 - 500° C is reached. At higher pyrolysis temperatures, the fraction of sulfur that is volatilized decreases with increasing temperature. At a temperature of 450° C and a pyrolysis time of fifteen seconds the maximum amount of released sulfur was observed. This release totaled about forty per cent of the sulfur contained in the liquor as thiosulfate. Longer pyrolysis times at this temperature, which were obtained by subjecting liquor samples to an additional heating cycle, did not result in significant additional sulfur release.

Table 13. Pyrolysis of thiosulfate-containing soda liquor.
65.2% solids liquor; 6.0 - 8.7 mg solids sample size

No. of Tests	Time at Temp. (sec)	Ave. Temp. (°C)	Sulfur Released (mg S/100 g solids) (± 95% C.L.)	(per cent)[a] (± 95% C.L.)
10	4.5	274	141 ± 84	4.70 ± 2.80
10		327	331 ± 141	11.03 ± 4.70
10		448	876 ± 180	29.20 ± 6.00
7		513	844 ± 49	28.13 ± 1.63
17		566	658 ± 89	21.93 ± 2.97
14	9.0	438	933 ± 42	31.10 ± 1.40
11		514	1074 ± 89	35.80 ± 2.97
11		573	856 ± 92	28.53 ± 3.07
10	10.5	277	233 ± 96	7.77 ± 3.20
10		326	416 ± 132	13.87 ± 4.40
10		451	1079 ± 130	35.97 ± 4.33
10		555	719 ± 107	23.97 ± 3.56
10		734	397 ± 109	13.23 ± 3.63
10	15.0	276	267 ± 104	8.90 ± 3.47
10		328	578 ± 104	19.27 ± 3.47
10		453	1302 ± 114	43.40 ± 3.80
10		563	744 ± 119	24.80 ± 3.96
10		732	392 ± 67	13.07 ± 2.23

[a] Initial thiosulfate content based on Table 10

The results obtained by this study are similar to those obtained by Douglas and Price's[30] pyrolysis of thiosulfate with soda lignin and Strohbeen and Grace's[31] pyrolysis of thiosulfate with vanillic acid. The results obtained by Strohbeen and Grace for thiosulfate pyrolysis with sodium gluconate are somewhat lower than the present study's results; the results of Douglas and Price's pyrolysis of thiosulfate with glucose are much higher. The results of TGA studies suggest that lignin is the major component of the black liquor that is being decomposed during black liquor pyrolysis.[15] Therefore, it would be expected that the present study's results would most closely resemble results of studies using model compounds that resembled kraft lignin (soda lignin and vanillic acid).

PYROLYSIS OF SODIUM SULFIDE

The results of pyrolysis experiments on soda black liquor containing sodium sulfide are summarized in Table 14. Individual test results are shown in Table 26, Appendix 2. Because the liquor also contained some thiosulfate, it was necessary to separately account for the sulfur that was released by each sulfur species. This task was accomplished by measuring the liquor's sulfide and thiosulfate contents during the time the pyrolysis tests were being performed. Then, using the model developed for sulfur release from sodium thiosulfate (see below), the fraction of the total sulfur release that could be attributed to the thiosulfate was calculated and subtracted from the total amount of sulfur volatilized. In performing these calculations, it was assumed that the sulfur released from thiosulfate and sulfide were additive. This assumption is verified below in the section titled "Verification of Pyrolysis Kinetics Model"

The results of these calculations are shown in Table 15. These results show that, although the total amount of sulfur that can be released from sulfide is similar to the amount that can be volatilized during pyrolysis of thiosulfate, the temperature dependency exhibited by the sulfide release

Table 14. Pyrolysis of sulfide-containing soda liquor. 66.7% solids liquor; 6.2 - 8.2 mg solids sample size

No. of Tests	Time at Temp. (sec)	Ave. Temp. (°C)	Sulfur Released (mg S/100 g solids) (± 95% C.L.)
7	4.5	319	141 ± 107
5		369	329 ± 97
8		426	821 ± 303
9		474	873 ± 145
6		536	612 ± 111
7		684	271 ± 70
6	9.0	324	322 ± 139
7		373	418 ± 202
8		441	941 ± 297
16		471	1083 ± 104
5		518	705 ± 240
7		679	231 ± 64
6	15.0	324	292 ± 112
5		374	686 ± 382
9		426	1053 ± 231
9		480	990 ± 156
6		542	689 ± 183
7		678	263 ± 102

reactions is somewhat different than that shown by the reactions of thiosulfate. Release of sulfur from sulfide is not significant until pyrolysis temperatures of above three hundred degrees are reached. However, at temperatures above three hundred, the amount of sulfur released reaches its maximum value quite rapidly. The decline in release from sulfide at higher temperatures is also much more rapid than is the case with thiosulfate.

It should also be noted that, although the average maximum amounts of sulfur that can be released during pyrolysis of thiosulfate- and sulfide-containing liquors are similar, the results of the sulfide pyrolysis tests show greater variability than do the results of thiosulfate pyrolysis. For the

Table 15. Calculated release from sulfide-containing liquor.
Sulfur Released in mg S/100 g solids
(Per cent refers to per cent of major sulfur species)

Time (sec)	Temp. (°C)	Sulfur Released Total	From $S_2O_3^{2-}$	From S^{2-}	Per cent (from S^{2-})
4.5	319	141	34	107	5.12
	369	329	64	265	12.68
	426	821	109	712	34.07
	474	873	141	732	35.02
	536	612	124	488	23.34
	684	271	76	195	9.33
9.0	324	322	63	259	12.39
	373	373	104	269	12.87
	441	941	168	773	36.99
	471	1083	182	901	43.11
	518	705	160	545	26.07
	679	231	78	153	7.32
15.0	324	292	94	198	9.47
	374	686	149	537	25.69
	426	1053	186	867	41.48
	480	990	203	787	37.66
	542	689	147	542	25.93
	678	263	79	184	8.80

thiosulfate-containing liquor, all the pyrolysis tests result in sulfur releases totaling fifty per cent or less of the total sulfur present as thiosulfate. Individual test measurements of sulfur release from sulfide-containing liquor, on the other hand, are frequently above fifty per cent of the sulfur present as sulfide, with some measurements reaching values of over sixty per cent. These results indicate that, under certain circumstances,

substantially more sulfur can be volatilized from sulfide than the amount indicated by the maximum average release.

The results shown above are similar to those obtained by Douglas and Price[30] for pyrolysis of sodium sulfide with soda lignin. However, the present study's results are quite different from results obtained by Douglas and Price for pyrolysis of sodium sulfide with glucose. The results also differ greatly from those reported by Strohbeen and Grace[31] for the pyrolysis of sodium sulfide with sodium gluconate and vanillic acid. Strohbeen and Grace found that almost all the sulfide sulfur was released to the gas phase when sodium sulfide was pyrolyzed with either of the organic compounds. However, the present study shows that, on the average, less than one-half of the sulfur is released during pyrolysis.

PYROLYSIS OF ORGANIC SULFUR

Pyrolysis tests were peformed using the liquor formulated to contain only organic sulfur. Although measurable sulfur releases were obtained from pyrolysis of this liquor, the results of the tests did not allow meaningful conclusions to be drawn about its sulfur release characteristics during pyrolysis. The test results exhibited wide and unsystematic variations. At least part of the cause of these variations was the small amount of organic sulfur present in the liquor and the resulting small release of sulfur-containing gas during pyrolysis. These small releases were difficult to measure accurately using the technique described above for determining sulfur release. Also, the concentration of organic sulfur was not determined by a direct test, but was instead calculated from the difference between the

measured total sulfur and the sum of the sulfate, sulfite, thiosulfite, and sulfide concentrations. Because of possible errors in the determinations of the inorganic sulfur or total sulfur concentrations, or the presence of other sulfur species for which no analysis was done, it is possible that the liquor's true organic sulfur content is quite different from the calculated value. These uncertainties about the actual amount of organic sulfur present in the liquor, compounded by the wide variation in test results made it impossible to accurately determine the amount of sulfur volatilized from black liquor containing organic sulfur during pyrolysis.

SUMMARY OF PYROLYSIS TESTS RESULTS

The results of the pyrolyis tests have shown that, of the four major inorganic sulfur species present in kraft black liquor, two, sodium sulfate and sodium sulfite, release only minor amounts of sulfur when pyrolyzed in the presence of soda black liquor. The other two species, sodium thiosulfate and sodium sulfide, can release forty per cent of their sulfur during pyrolysis. These results are similar to those obtained by Douglas and Price[30] for pyrolysis of the same inorganic sulfur species with soda lignin. However, the amounts of sulfur released from either thiosulfate- or sulfide-containing soda liquor is considerably less than the sulfur release from kraft liquor reported by Feuerstein[29] and Jones[17]. Volatilization of seventy per cent or more of a liquor's total sulfur was reported by both researchers. Reasons for the differences between the amount of released sulfur reported by Feuerstein and Jones and that observed in the present study will be discussed in the section entitled "VERIFICATION OF OVERALL DROP MODEL".

HEAT TRANSFER TO BLACK LIQUOR DROPS

The data gathered from the heat transfer experiments were used to generate profiles showing the external and internal temperature of a pyrolyzing black liquor particle as a function of time. A graph showing the results of a typical test is shown in Fig. 5. The surface temperature measurement remains constant for the first part of the test. The pyrometers inability to measure the temperature during the first part of the run results from the changes in the emissivity of the liquor particle during pyrolysis. Prior to each set of runs the optical pyrometer was calibrated by focusing it on a pyrolyzed particle in the reactor whose temperature has come to equilibrium. The pyrometer's emissivity setting is then adjusted until the temperature indicated by the pyrometer is identical to that indicated by the thermocouple. The typical emissivity found to be appropriate was 0.55. This calibration procedure resulted in the instrument's ability to measure temperatures during only the latter stages of the experimental run.

The measurements of the outer and inner temperatures of the black liquor drops were used to prepare time - temperature plots similar to the one shown in Fig. 5. These plots were then used to test and modify the heat transfer model as described in the section entitled "HEAT TRANSFER MODEL", below.

EFFECT OF PARTICLE SIZE, SOLIDS CONTENT, AND SWELLING CHARACTERISTICS

The results of the swelling determination tests are shown in Table 16. The swelling reported is defined as the volume of the fully swollen, pyrolyzed drop (in cc) divided by the drop's original mass of solids (in grams). The amount of swelling a black liquor drop undergoes during pyrolysis decreases

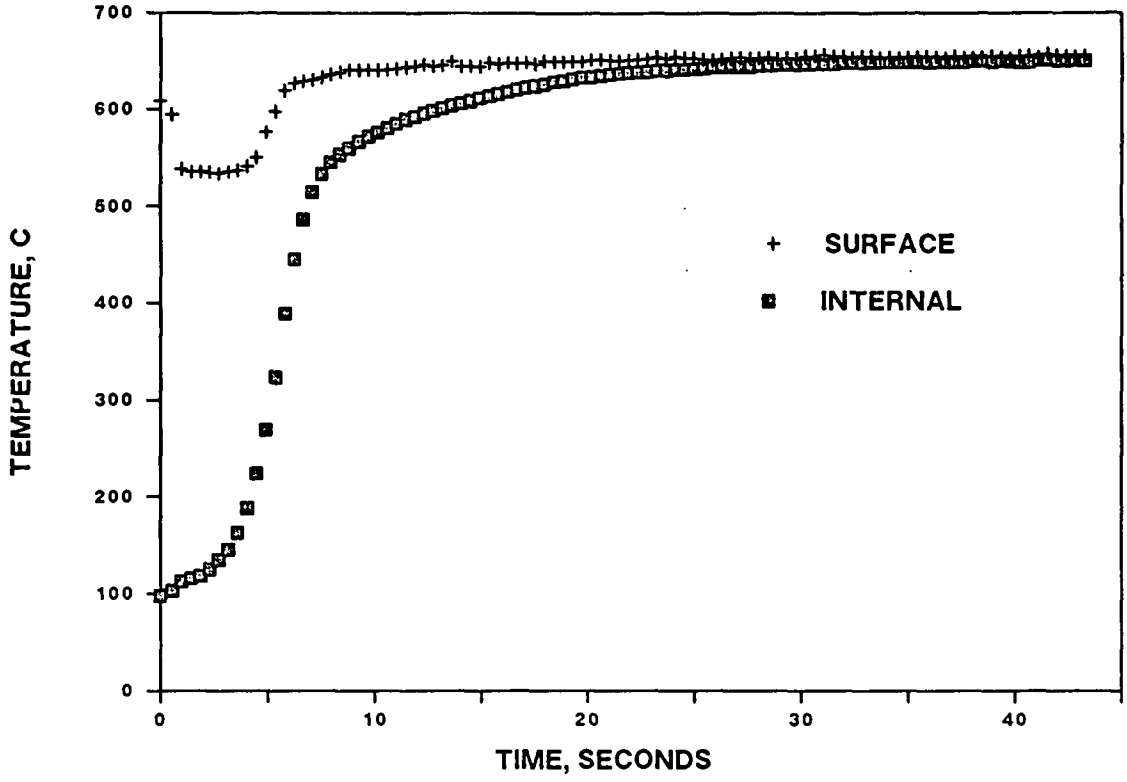

Fig. 5. Black liquor pyrolysis - surface and internal temperatures; 8.6 mg drop, 66.9% solids.

somewhat with increasing solids content. Addition of a swelling retardant greatly decreased the amount of swelling that the particle undergoes.

Table 16. Swelling characteristics of kraft black liquors. (Nominal Gas Temperature: 800° C)

Liquor Solids (%)	Swelling (± 95% C.L.) (cc/g solids)
62.7	55.5 ± 12.2
66.9	51.7 ± 6.0
74.0	46.0 ± 7.1
74.0[a]	23.8 ± 2.8

[a] Swelling retardant added

The results of pyrolysis tests done in the radiant single particle reactor are shown in Table 17. A regression analysis was performed on the results obtained to determine which of the three variables significantly affected sulfur release. As independent measurements for particle size, but not for solids content or degree of swelling had been made for each individual test, the analysis had to be performed in several steps. First, using all sixty-three tests (3 liquors x 3 drop sizes x 7 tests at each drop size), the amount of sulfur released was regressed against drop size and a dummy variable (1,2,or 3) corresponding to the three different liquors. The results of this test indicated that both drop size and liquor number had significant impacts on the amount of sulfur released.

Table 17. Effect of particle weight solids content, and degree of swelling on sulfur release during black liquor pyrolysis. (Gas Temperature = 665° C)

Solids (%)	Swelling (cc/g solids)	Particle Weight (mg solids)	Sulfur Release (mg S/100 g solids) (± 95% C.L.)
63.4	55.5	6.5	546 ± 53
		12.6	541
		24.7	810
77.7	46.0	7.9	608 ± 51
		14.9	754
		30.7	891
76.7	23.8	7.9	643 ± 60
		14.9	731
		29.4	874

The next step was to determine which of the characteristics of the different liquors (solids content and degree of swelling) were significant. An average sulfur release was calculated for each of the three liquors and this

average regressed in separate tests against solids content and degree of swelling. The results of these tests indicated that changing the liquor's solids content significantly affected the amount of sulfur released, but that altering the swelling characteristics of the liquor had no significant impact on the amount of sulfur volatilized.

Finally, the sulfur releases and drop sizes from the individual tests and the average solids contents of the three liquors were used to develop a regression equation that would predict sulfur release as a function of drop size and solids content. The equation predicting sulfur release as a function of particle size and solids content is:

$$Rel = 87.5 + 12.3 * Wt + 5.77 * Sol \quad (36)$$

where:

Rel = Sulfur release (mg S/100 g solids)

Wt = Drop size (mg solids)

Sol = Solids (%).

The model has a coefficient of determination (R^2) value of 0.49, which means that less than half of total variation in the release data is accounted for by the regression model.

It should be noted that this model, while useful in predicting trends in sulfur release, is not a true multiple regression model as it was developed using the assumption that the solids content was independently measured for each test. It should also be emphasized that the equation developed is specific to the liquors used in the tests. Liquors having different sulfur contents will release amounts of sulfur that differ from those predicted by the regression model.

The results shown in Table 17 are quite different from those obtained by Cantrell[22] for burning drops of various sizes and solids content in air. Cantrell found that increasing the liquor's particle size or solids content resulted in a decrease in the amount of sulfur released, while the results from the present study indicate that more sulfur is released during pyrolysis of larger or higher solids drops. However, consideration of the processes occurring during black liquor burning versus those that take place when the drop is pyrolyzed suggests that the results obtained by the two studies are reconcilable. Cantrell hypothesized that a layer of molten smelt formed on the outside of the black liquor particles during the combustion of volatiles. This smelt layer then captured the sulfur being released from the drop's inner regions. During the pyrolysis experiments conducted, however, the drop temperature is below the melting point of many of the liquor's inorganic salts. Therefore, there is no outer smelt layer available to capture sulfur being released from the particle's interior. Also, it is known that black liquor drops swell to a greater extent during pyrolysis than do similar particles during burning.[62] Thus, even if pyrolysis temperatures were high enough to melt the liquor's inorganic salts, a larger fraction of the particle's mass would be present on or near the surface of the particle during pyrolysis than would be the case during burning of the drop. Therefore, there will be less opportunity for the volatilizing sulfur gases to encounter molten smelt and be captured. Finally, it is possible that large drops, or those with high solids, will burn hotter than will small or low solids drops. These particles would thus spend less time at the lower temperatures at which sulfur release is at a maximum. During pyrolysis of large or high solids drops, on the other hand, more time is spent at lower temperatures than is the case for small or low

solids particles.

The fact that changes in the swelling characteristics of the liquor had no significant effect on the amount of sulfur volatilized is surprising. It would be expected that the difference in particle size during pyrolysis would greatly change the rate of the drop's temperature rise. However, comparisons of temperature profiles of swelling and nonswelling drops of similar size and solids content show little difference in the time required to reach a certain temperature. Because the drops' time-temperature histories are similar, the difference in the amounts of sulfur released by the drops should be minimal.

Also, the volatile sulfur contained in the liquors tested was mainly thiosulfate, which may explain the lack of difference in sulfur release observed between liquors having normal and reduced swelling characteristics. Since thiosulfate releases its sulfur much more slowly than does sulfide, any differences in the drop's heating behavior caused by changes in swelling characteristics will not be as strongly reflected in a liquor which contains most of its volatile sulfur as thiosulfate. Had the sulfur in the liquor been primarily sulfide, a difference in sulfur release levels may have been observed.

SULFUR RELEASE MODEL

MODELING OBJECTIVES

The test results discussed above allow the formulation of a model predicting the amount of sulfur volatilized from a black liquor drop undergoing pyrolysis in an inert atmosphere. The results of the pyrolysis kinetics experiments can be described with kinetic equations that predict the amount of sulfur released during pyrolysis as a function of time, temperature, and the liquor's sulfur content. From the results of the heat transfer experiments, the time temperature history of a black liquor drop can be described as a function of its physical characteristics (size, solids, swelling) and the environment in which the drop is heated. Combining the equations that calculate drop temperature with those describing sulfur release kinetics will result in an overall predictive model describing sulfur release during pyrolysis of a black liquor drop.

PYROLYSIS KINETICS MODEL

First Order Decomposition Model

A common method used to model pyrolysis reaction kinetics is to treat the volatilization reactions as a single first order decomposition[41]. The amount of volatiles (or, one or more of the products of pyrolysis), appearing as a function of time and temperature, is expressed as

$$dV/dt = K(V^* - V) \qquad (37)$$

where:

V = amount of volatiles emitted at time t (usually expressed as a fraction of initial volatiles content)

V^* = maximum fraction that can be volatilized

K = rate constant.

The rate constant, K, is usually correlated using an Arrhenius-type expression:

$$K = K_0 e^{-E/RT} \tag{38}$$

where:

K_0 = pre-exponential factor

E = activation energy

R = ideal gas constant

T = absolute temperature.

Separating the variables yields:

$$\int_0^V dV/(V^* - V) = \int_0^t K dt \tag{39}$$

which can be solved for the amount of volatile sulfur emitted to yield:

$$V = V^* - V^* \exp(-\int_0^t K dt) \tag{40}$$

where the integral describes the time-temperature history to which the liquor is subjected.

During pyrolysis tests the liquor was heated to the desired pyrolysis temperature, held at that temperature for the chosen time interval, and allowed to cool. Although the heating was very rapid, significant amounts of sulfur could be emitted during the non-isothermal portions of the run. To account for the sulfur released during these heating and cooling times, it was assumed that the rate of temperature rise or fall was linear. Examination of the graphs of the temperature profiles showed this assumption to be reasonable for the pyrolysis experiments, especially for the portions

of the curves that were at temperatures above 250° C, where sulfur release reactions occur. Using this assumption allowed Eq. 39 to be recast as[44]:

$$\int_0^V dV/(V^* - V) = \int_{250}^T (K/m)dT \qquad (41)$$

where m = dT/dt, the rate of temperature rise or fall. For the pyrolysis experiments, m was equal to 3973° C/sec during heating and 84° C/sec during cooling. The right-hand side of equation 41 was integrated using the trapezoid rule and included in the expression used to calculate the amount of sulfur volatilized during pyrolysis.

The results of the pyrolysis experiments on the soda liquor to which various sulfur species had been added were examined with the view of fitting such a first order decomposition model to the sulfur release data. Pyrolysis of liquors containing sodium sulfate or sodium sulfite resulted in release of very small amounts of sulfur. Because the contribution to a kraft liquor's overall sulfur release from either of these species will be insignificant, both sodium sulfate and sodium sulfite were modeled as being stable with respect to sulfur release during black liquor pyrolysis. The small amount of sulfur present in the liquor containing only organic sulfur and the wide variation in the results of the experiments performed on the liquor made interpretation of the results extremely difficult. Therefore, no attempt was made to model organic sulfur pyrolysis.

Thiosulfate Model

Examination of the results obtained from the pyrolysis of thiosulfate-containing liquor revealed that a first order decomposition model would not, by itself, adequately describe the release of sulfur during pyrolysis. The

first order decomposition model predicts a rise in the amount of sulfur released during a given pyrolysis time with increasing temperature until an upper limit (V^*) is reached. Once this level of volatilized sulfur is reached, further increases in temperature have no effect on the amount of sulfur given off during pyrolysis. For the thiosulfate-containing liquor, however, the amount of sulfur that is volatilized during pyrolysis decreases when the pyrolysis temperature is above a level of approximately five hundred degrees C. This type of behavior during black liquor pyrolysis has been observed in other pyrolysis studies[17,19,20].

Several different approaches were considered to explain these observations. The first of these was to hypothesize the existence of a capture reaction. In this reaction, some species in the pyrolyzing black liquor would react with the escaping sulfur-containing gases and convert them to a condensed sulfur species. It is known that molten sodium salts react rapidly with hydrogen sulfide to convert it to sodium sulfide[63]. Cantrell[22] hypothesized that the formation of such a molten layer on the outer surface of a burning droplet aided in capturing the sulfur being volatilized from the interior of the droplet. However, there are some objections to modeling the results obtained in this manner. First, the experimental apparatus is constructed in such a way that the black liquor is pyrolyzed as a very thin film. Thus, there would be little opportunity for sulfur-containing gases to come in contact with other compounds in the black liquor after they are generated. Second, the temperature at which the sulfur release begins to decline is well below the melting points of most inorganic salts found in black liquor.

The second method considered was to model the decline in sulfur release with increasing temperature as resulting from a competing reaction. This reaction would transform the volatile sulfur species (thiosulfate or sulfide) into one which did not release sulfur during pyrolysis. Several of the reactions that sodium thiosulfate is believed to undergo during pyrolysis result in formation of sodium sulfate, which is stable under pyrolysis conditions. This method of modeling the decline of sulfur release with increasing temperature, however, also has some objections. Strohbeen[5] has shown that sodium sulfide is the major sulfur species remaining in char after pyrolysis of either sodium thiosulfate or sodium sulfide in the presence of model compounds. Little or no sodium sulfate or sodium sulfite was found in the pyrolysis residue resulting from pyrolysis of either thiosulfate or sulfide. Thus, it is difficult to hypothesize the identity of the stable compound to which the thiosulfate or sulfide would be converted. Also, the results obtained from the present pyrolysis experiments make modeling them as the results of competing chemical reactions difficult. The data obtained show that as the pyrolysis temperature increases above 500^{o} C, the amount of sulfur released at a certain pyrolysis temperature tends to approach a constant value, regardless of the pyrolysis time. This type of behavior is not consistent with the expected results that would be obtained from competing reactions.

A third method that could be used to explain the behavior of the liquor at high temperatures is to employ thermodynamic considerations. As was noted earlier, the equilibrium composition resulting from the reaction that is assumed to a the major producer of sulfur gas:

$$Na_2S + H_2O + CO_2 \Rightarrow Na_2CO_3 + H_2S \quad (3)$$

shifts to the left at high temperatures, resulting in lower sulfur volatilization at higher temperatures. However, the experimental apparatus used in the pyrolysis experiments did not allow an equilibrium to be established between the gaseous and condensed sulfur species, as the sulfur-containing gases were constantly being removed by the nitrogen purge.

The method chosen to correlate the data for the high temperature pyrolysis tests was to modify the maximum amount of sulfur that could be released during pyrolysIs, V^*, by an empirical parameter, F, which was defined as the fraction of V^* that can be emitted at a given temperature. This parameter was assumed to be a function of temperature of the form

$$\ln(F) = A/T + B \quad (42)$$

where T is the absolute temperature and A and B are constants. At low temperatures (those for which the amount of sulfur released increases with increasing temperature), F is equal to 1.0. This method of describing sulfur release at higher temperatures results in a model that fits the observation made that, at high temperatures, the amount of sulfur released approaches a constant value, regardless of pyrolysis time. The model has the additional advantage that only five parameters are required to describe sulfur release throughout the range of temperatures employed in the pyrolysis experiments, as opposed to the six or more that would be necessary to model two reactions.

In order to determine the best values for the model constants, the results from the thiosulfate pyrolysis experiments were divided into two groups, those at low temperatures for which the sulfur released increased with increasing temperature, as would be predicted by a standard first order

decomposition model, and those at high temperatures, for which the amount of sulfur volatilized declined when the temperature was raised. The fraction of sulfur released, the pyrolysis time, and the temperature for the low temperature (<480^{o} C) tests, were passed to the program KT1. This program, a copy of which appears in Appendix 4, was written to find the best values of V*, K_0, and E. The program selects values of these constants, calculates the amount of sulfur released using Eqs. (39) and (41), and compares that value to the actual quantity of sulfur gas obtained during the experimental runs. The differences between the calculated and actual sulfur releases are squared and summed. The program searches for values of the three constants that will minimize this sum using a function minimization algorithm. For the low temperatue runs, the best values obtained were: $V^* = 0.4339$, $K_0 = 255.1$ sec^{-1}, and E = 10.49 kcal/mole.

Next, a program was written to search for the best values of A and B to be used to calculate F. This program, KT2, is found in Appendix 3. The results from experiments performed at high temperatures (>480^{o} C), for which the amount of sulfur released was declining with increasing temperature, were used as inputs into this program. The pyrolysis time, temperature and amount of sulfur released for each of the high temperature tests were passed to the computer program. For these tests, it was assumed that no sulfur was released during the cooling period. The program chose values for A and B and calculated the sulfur release expected during the constant-temperature portions of the run from the equation

$$V = V^* \exp(A/T + B)(1. - \exp(-K_0\ t \exp(-E/RT)) \qquad (43)$$

with the amount of sulfur released during heating being calculated in the

same manner as indicated above, except that the modified value of V^* is used. The total amount of volatilized sulfur thus calculated was compared to the measured release. The values for A and B that minimized the squared difference between the calculated and experimental values were determined by the program in the same method used in the program KT1. The best values for the two constants were found to be A = 3733.^{o} K and B = -4.957.

The results of the pyrolysis kinetics experiments compared to the model predictions are shown in Figs. 6 - 9. These graphs show the amount of sulfur volatilized from the thiosulfate-containing liquor as a function of temperature at various reaction times. The results of all the thiosulfate experiments are shown in Fig. 10, which compares the measured and calculated values.

Sulfide Model

The thiosulfate model thus obtained was used to calculate the amount of released sulfur from the sulfide-containing liquor that would be expected to result from thiosulfate pyrolysis. This amount of sulfur was subtracted from the total sulfur release from the sulfide-containing liquor for each test. The corrected sulfide releases were then modeled using a method similar to that described above for describing the thiosulfate results.

The programs used to calculate the constants for the sulfide model are shown in Appendix 4. The program that determined the values of V^*, K_0, and E for the sulfide tests is named KS1 and is similar to the program KT1 used to calculate model parameters for the thiosulfate data. The best values found for the model's parameters were V^* = 0.4020, K_0 = 9.69 x 10^6 sec^{-1}, and E =

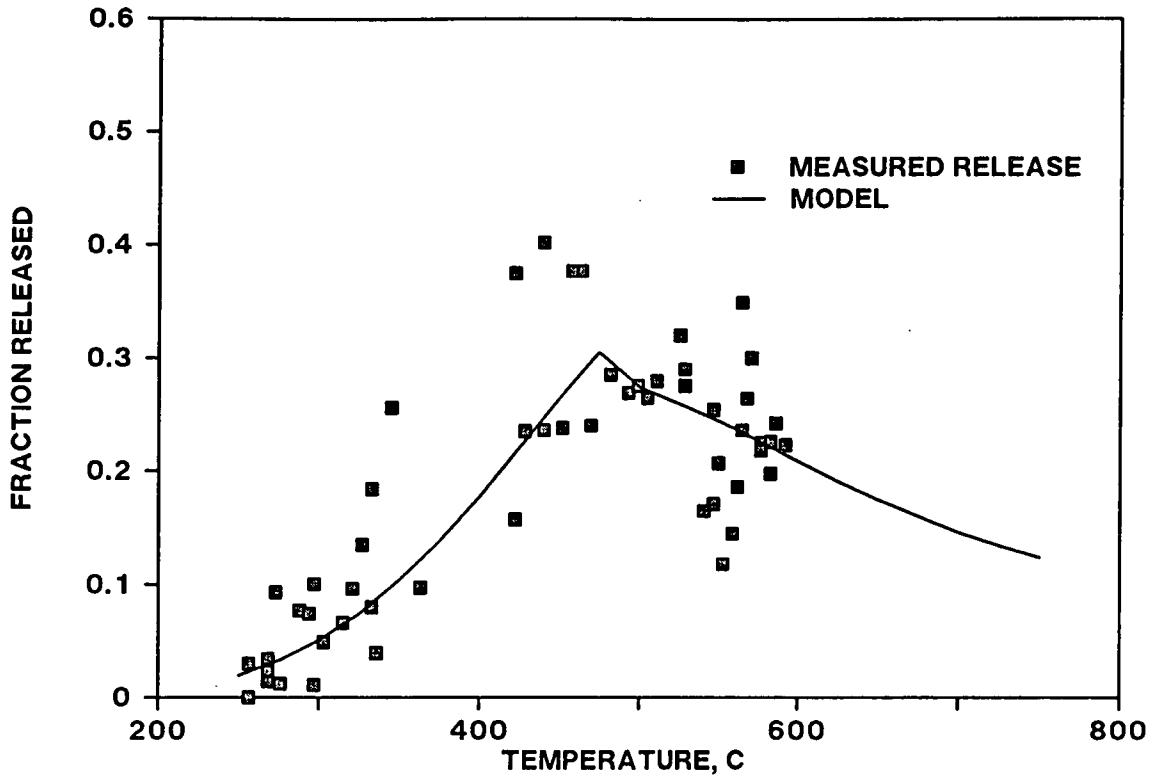

Fig. 6. Thiosulfate release model - 4.5 seconds.

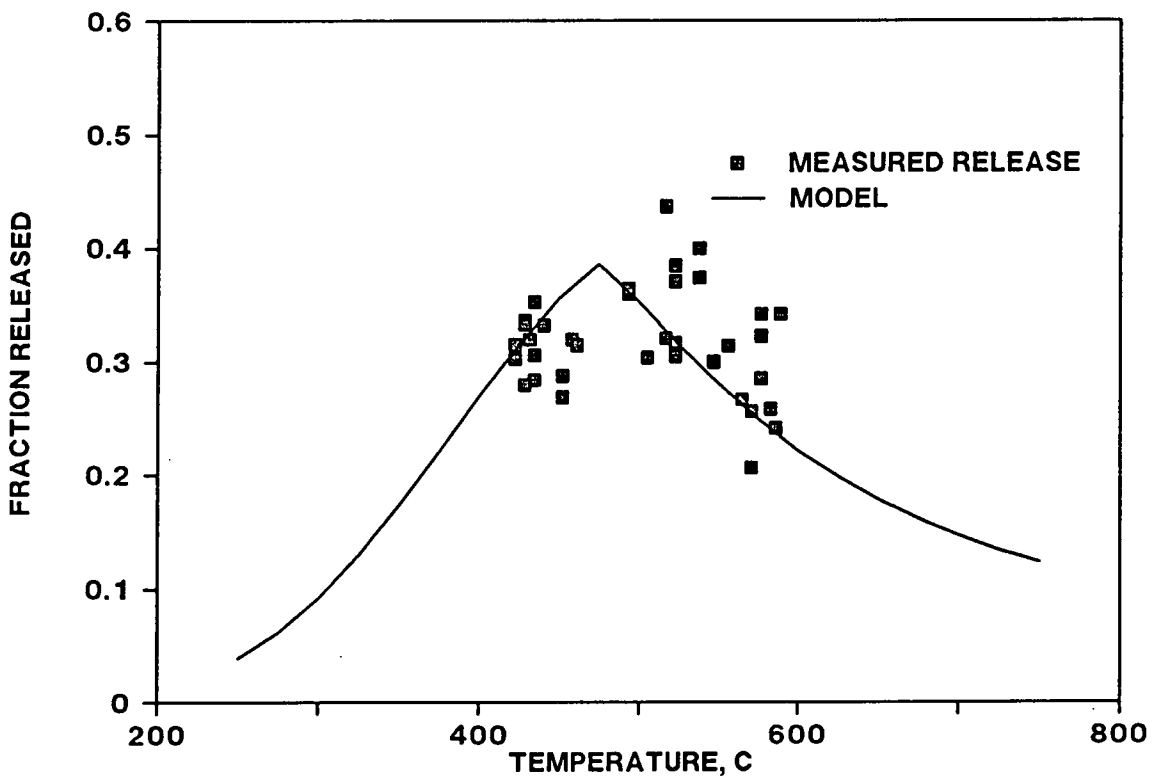

Fig. 7. Thiosulfate release model - 9.0 seconds.

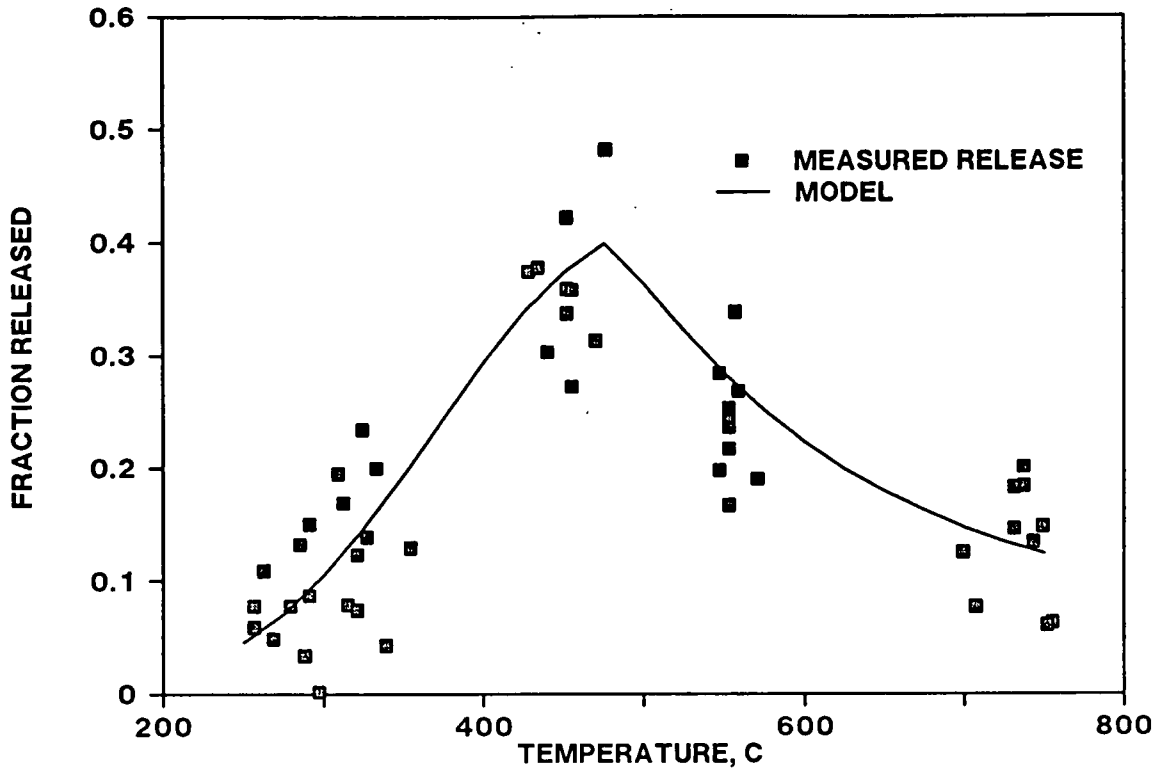

Fig. 8. Thiosulfate release model - 10.5 seconds.

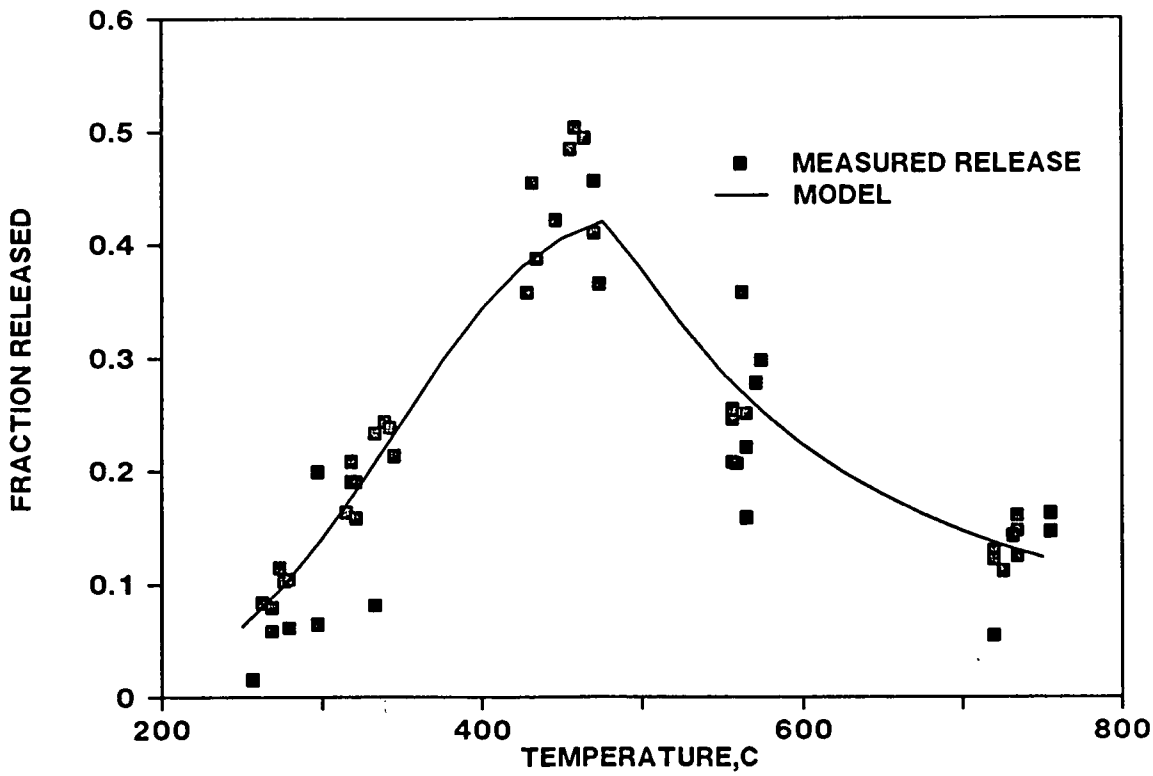

Fig. 9. Thiosulfate release model - 15.0 seconds.

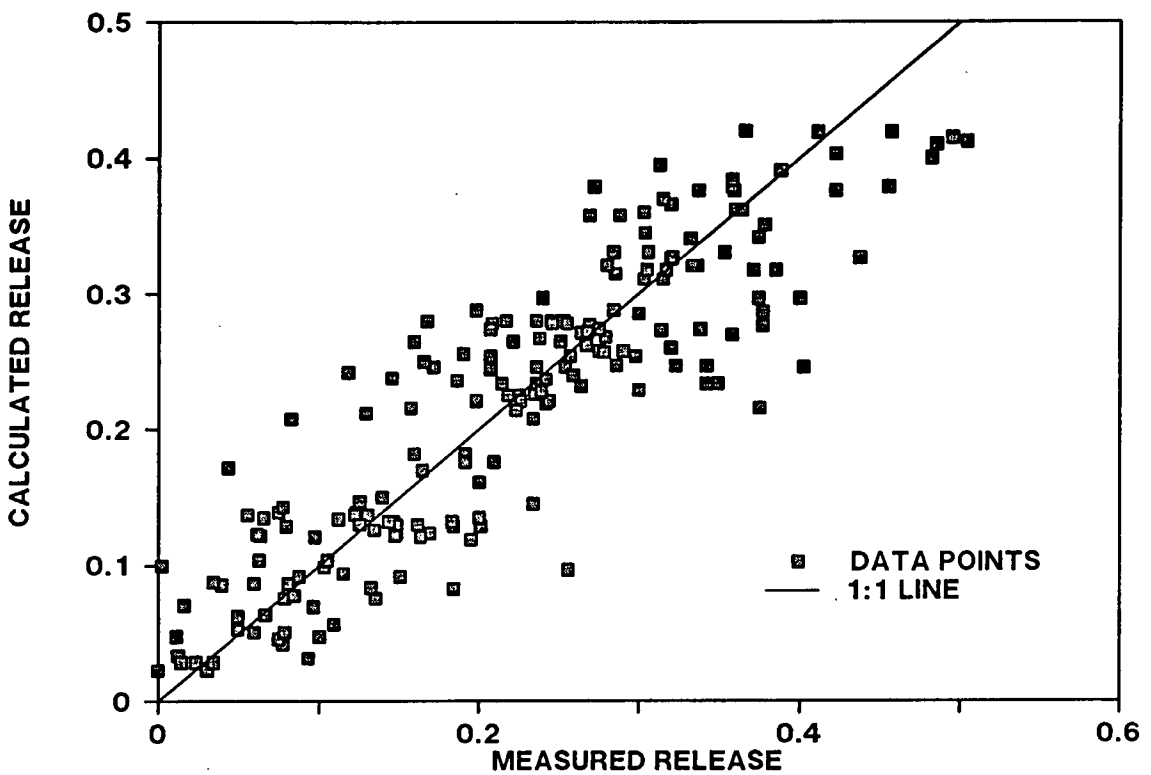

Fig. 10. Thiosulfate release model - measured vs predicted.

24.10 kcal/mole. For pyrolysis tests that were performed at temperatures above 490^{o} C, at which point the sulfur release began to decline, another program, similar to KT2, was written to calculate the constants A and B for the sulfide data. A copy of this program, called KS2, appears in Appendix 4. The values returned by the program for these parameters were A = 7497.^{o} K and B = -9.785. Figs. 11 - 13 show the results of the model compared to the experimental values. Results from all the tests compared to predicted values are shown in Fig. 14.

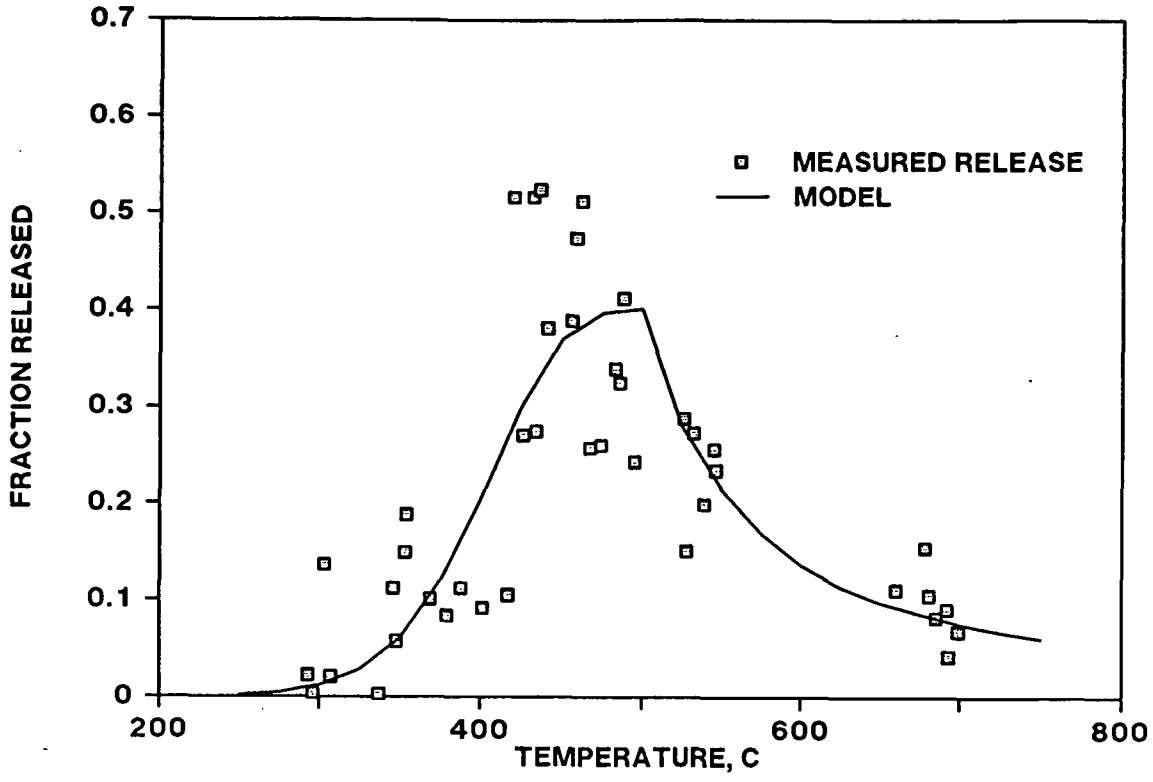

Fig. 11. Sulfide release model - 4.5 seconds.

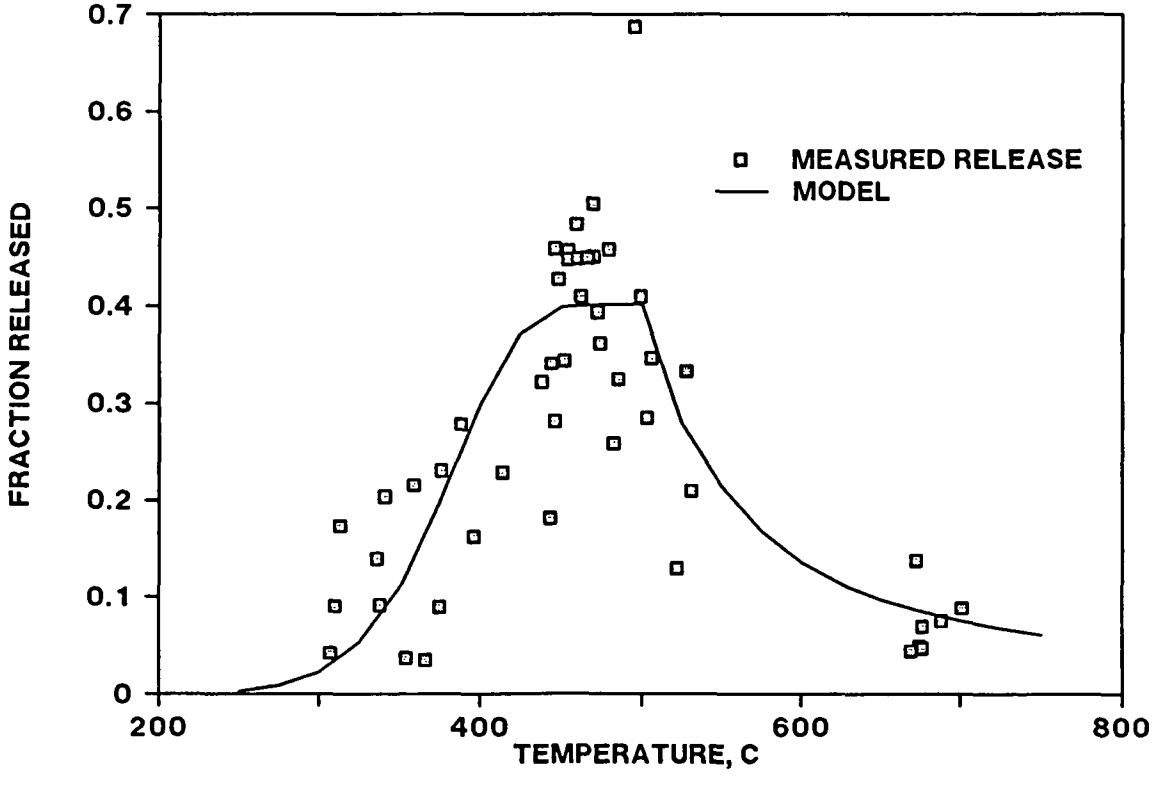

Fig. 12. Sulfide release model - 9.0 seconds.

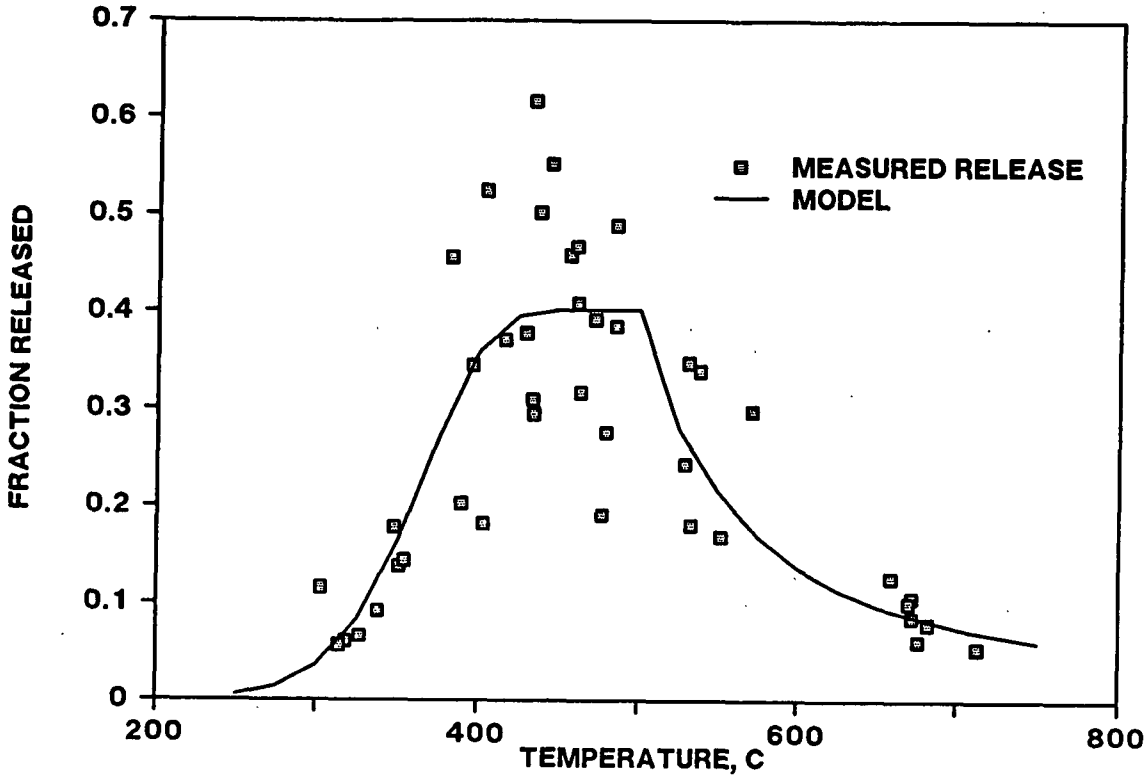

Fig. 13. Sulfide release model - 15.0 seconds

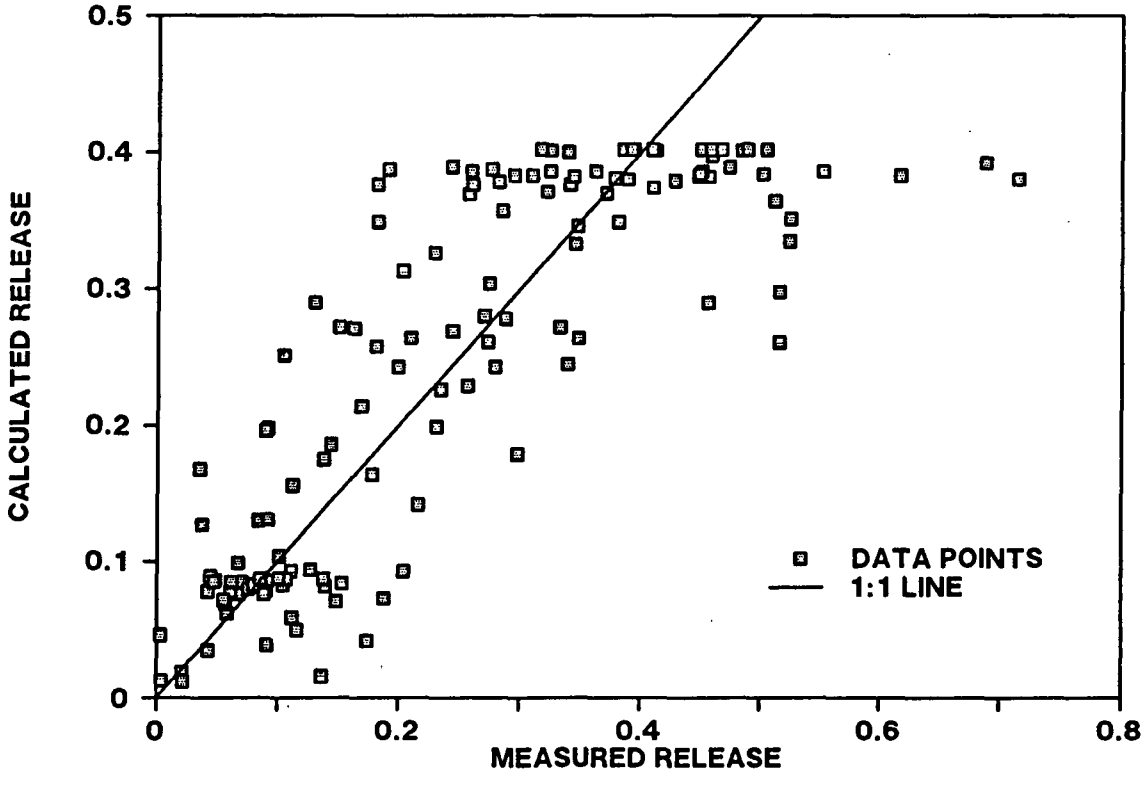

Fig. 14. Sulfide release model - measured vs predicted.

Comparison of Thiosulfate and Sulfide Models

The results of the pyrolysis tests and the values calculated for the two models' constants show that both thiosulfate and sulfide can release similar amounts of sulfur during pyrolysis. However, the models indicate that the two sulfur-containing species behave quite differently while being pyrolyzed. The sulfide model's higher activation energy indicates that higher temperatures must be reached before significant amounts of volatilized sulfur will be seen from a liquor containing sulfide than will be the case for a black liquor whose sulfur is present as thiosulfate. However, the sulfide model's larger pre-exponential factor shows that the release of sulfur from sulfide is much faster than the release from thiosulfate for much of the temperature range studied. Because of this accelerated rate, a sulfide-containing liquor will reach its maximum amount of volatilized sulfur much faster than will a liquor containing thiosulfate. This increased rate accounts for the "plateauing" of the sulfide model in the 450 - 500^{o} C temperature range for all three pyrolysis times. The thiosulfate model, on the other hand, shows that the maximum release is only approached with the longest pyrolysis time (15 seconds) and at temperatures of approximately 480^{o} C. At higher temperatures, the amount of sulfur released from both sulfide and thiosulfate declines. The decline in sulfur released with higher pyrolysis temperatures is more rapid for the sulfide-containing liquor than for the liquor whose sulfur is present as thiosulfate. This trend is reflected in the sulfide model's larger value for the parameter "A".

The models' results also help to explain some of the scatter seen in the results of the pyrolysis tests. Undoubtedly, much of the scatter is simply

due to the stochastic nature of the sulfur release process. Other studies of sulfur release during pyrolysis with black liquor[21] or model compounds[5] present results with similar variations. However, some of the variation seen in the present study's results, especially the larger variation in the sulfide results relative to those for thiosulfate, are probably due to the fact that, for much of the temperature range studied, there are very large changes in the amount of sulfur released from sulfide with only minor differences in temperature. Thus, any small error in temperature measurement, or minor variations in the temperature at different locations on the wire screen used for heating the liquor could result in large differences in the amount of sulfur released at two seemingly identical temperatures.

Statistical Analysis of Pyrolysis Kinetics Models

After the models for predicting sulfur release from thiosulfate and sulfide were generated, a lack of fit test was used to examine the adequacy of the models. The individual test results that were generated at a single pyrolysis time and at approximately a single temperature were grouped together as if they were replicate tests at the average temperature. The differences between the sulfur release measured by the individual tests and that predicted by the model were used to calculate a residual sum of squares. This residual sum of squares was divided into two parts: the pure error sum of squares, which is a measure of the scatter of the data, and the lack-of-fit sum of squares, which estimates the error due to the model itself. The error sum of squares and lack of fit sum of squares were then used to calculate mean squares. The ratio of the lack-of-fit and error mean squares was examined using an F test to determine if there was significant lack of

fit in the pyrolysis kinetics model. The F values corresponding to ninety-five per cent confidence limits were 1.72 for the thiosulfate data and 1.81 for the sulfide data.

The results of this analysis are shown in Table 18. The complete analysis is shown in Tables 27 and 28, Appendix 2. These results indicate that there is significant lack of fit for the thiosulfate model, while the sulfide model shows no significant lack of fit. As a further test, the pure error mean square and the number of observations at each average temperature were used to calculate ninety-five per cent confidence limits on each of the average sulfur release values. The results of these calculations are shown in Figs. 15 - 21. The larger confidence limits shown for the sulfide data compared to the thiosulfate results indicate that the sulfur releases measured during the sulfide tests have much more scatter than do the release measurements obtained from thiosulfate pyrolysis. This larger degree of scatter translates to a much higher pure error mean square for the sulfide data, and results in a smaller F ratio, despite the sulfide model's larger lack-of-fit mean square. Because of the large variation in the sulfide results, it cannot be concluded that the sulfide model more accurately describes sulfur release than does the thiosulfate model; in fact the thiosulfate model may be a better representation of the true sulfur release rate from thiosulfate than is the sulfide model an accurate description of sulfur release from sulfide. Therefore, after examination of Figs. 15 - 21, it was concluded that, although the thiosulfate model's lack of fit is statistically significant, it is not practically significant and that the model adequately represents the results obtained in the pyrolysis kinetics

experiments.

Table 18. Statistical analysis of thiosulfate and sulfide models.

Thiosulfate Model

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F ratio
Regression	0.535	185	2.89×10^{-3}	
Lack of fit	0.088	13	6.80×10^{-3}	2.62
Pure error	0.446	172	2.60×10^{-3}	

Sulfide Model

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F ratio
Regression	1.067	128	8.34×10^{-3}	
Lack of fit	0.147	13	11.28×10^{-3}	1.41
Pure error	0.921	115	8.00×10^{-3}	

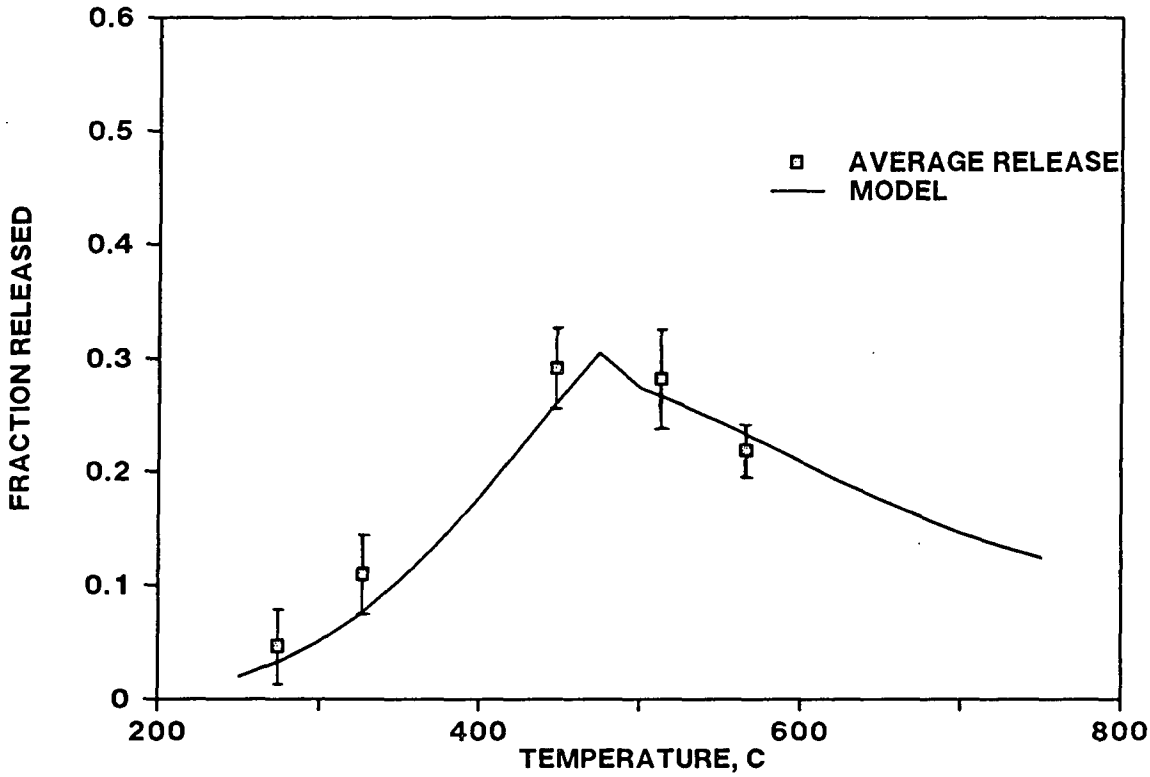

Fig. 15. Thiosulfate release - average values with 95% confidence limits; 4.5 seconds pyrolysis time.

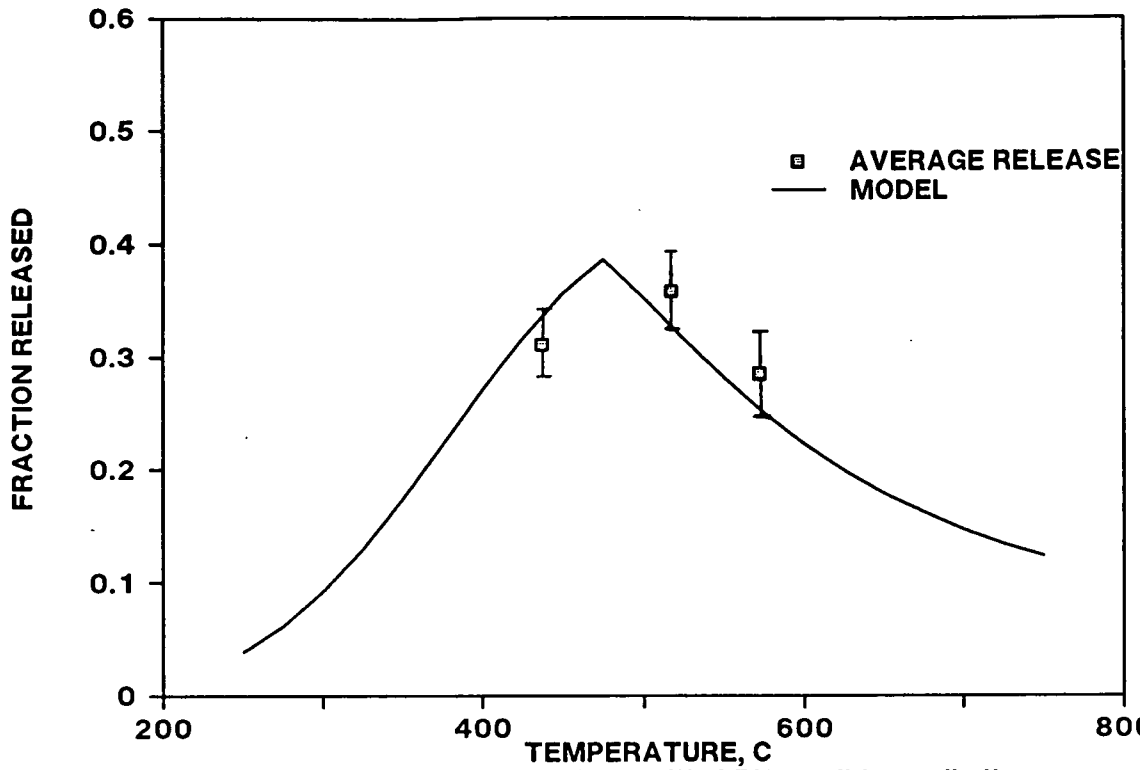

Fig. 16. Thiosulfate release - average values with 95% confidence limits; 9.0 seconds pyrolysis time.

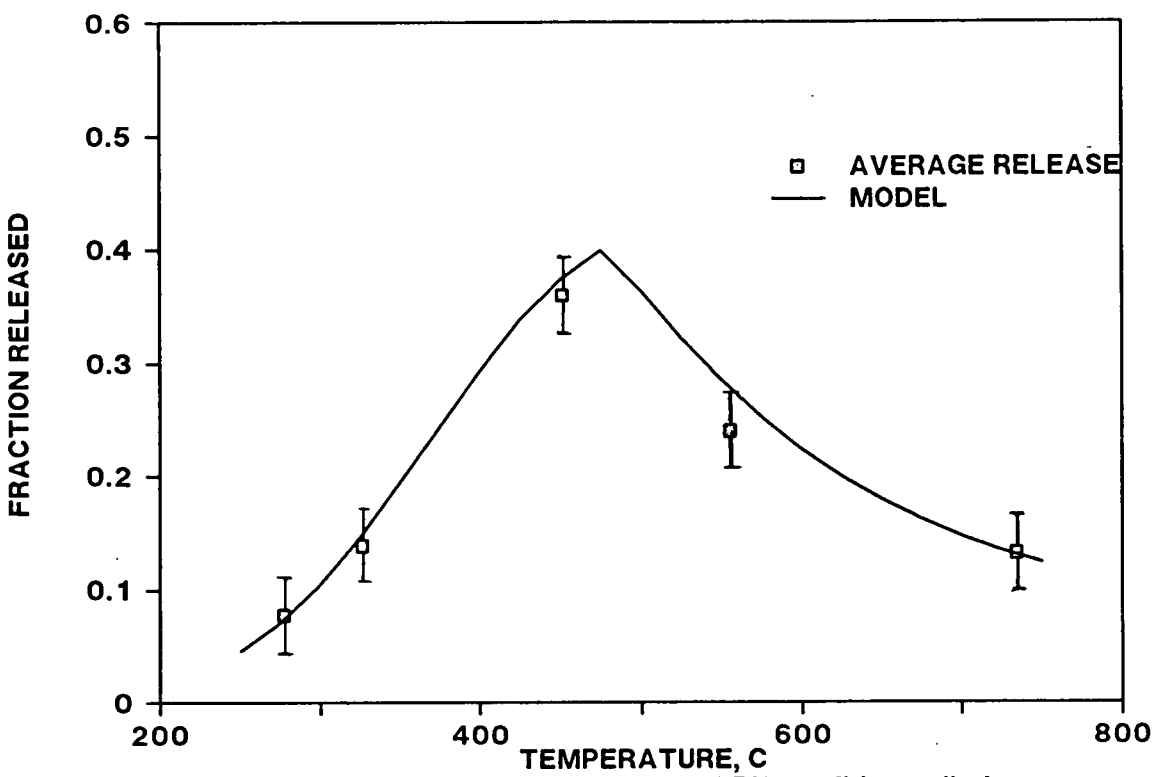

Fig. 17. Thiosulfate release - average values with 95% confidence limts; 10.5 seconds pyrolysis time.

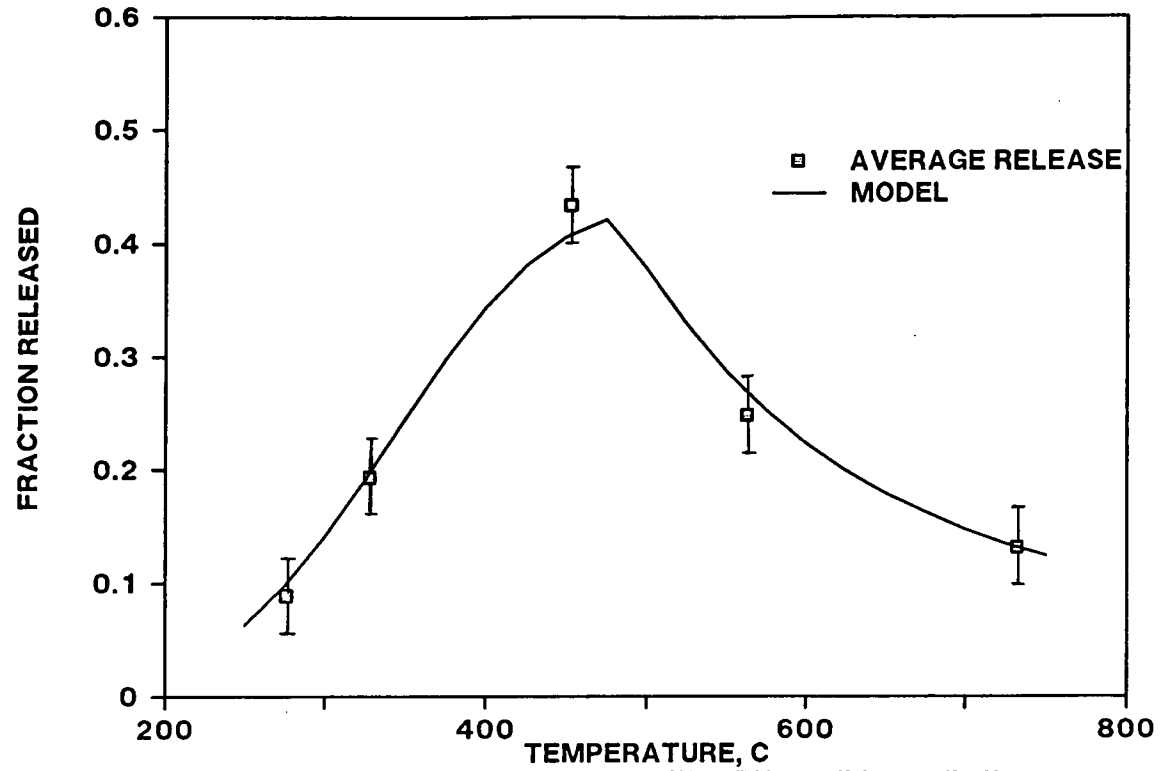

Fig. 18. Thiosulfate release - average values with 95% confidence limits; 15.0 seconds pyrolysis time.

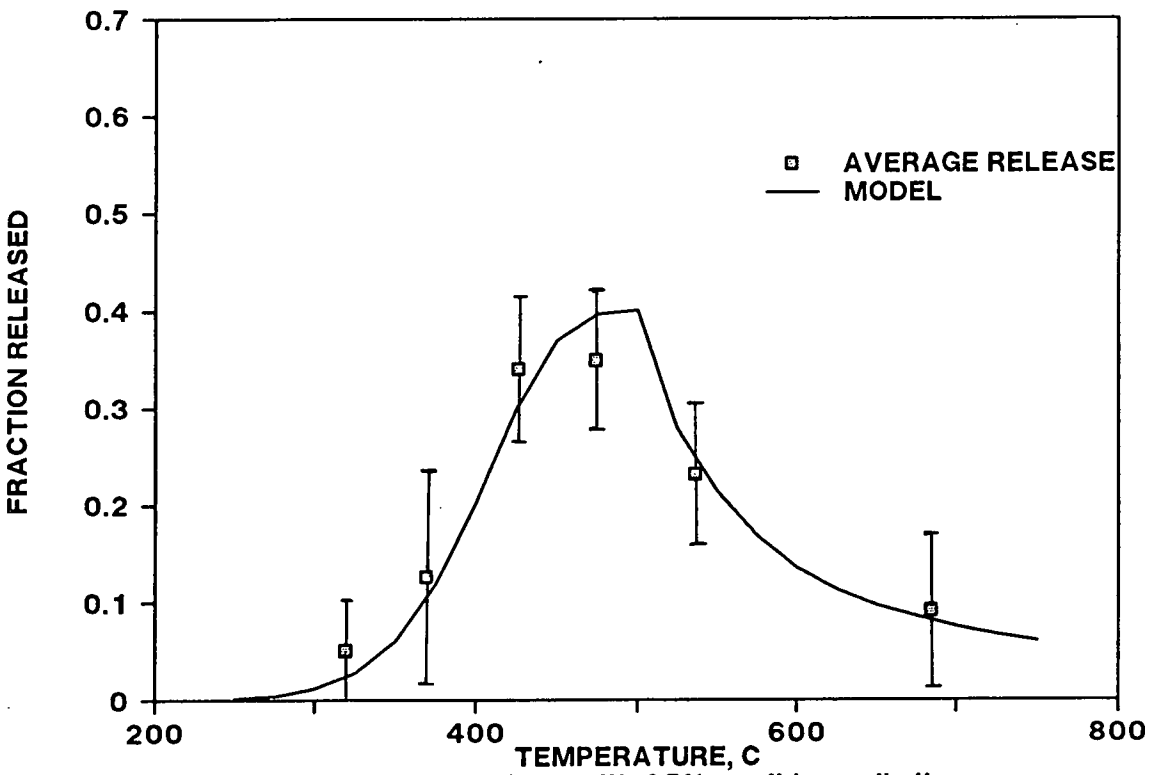

Fig. 19. Sulfide release - average values with 95% confidence limits; 4.5 seconds pyrolysis time.

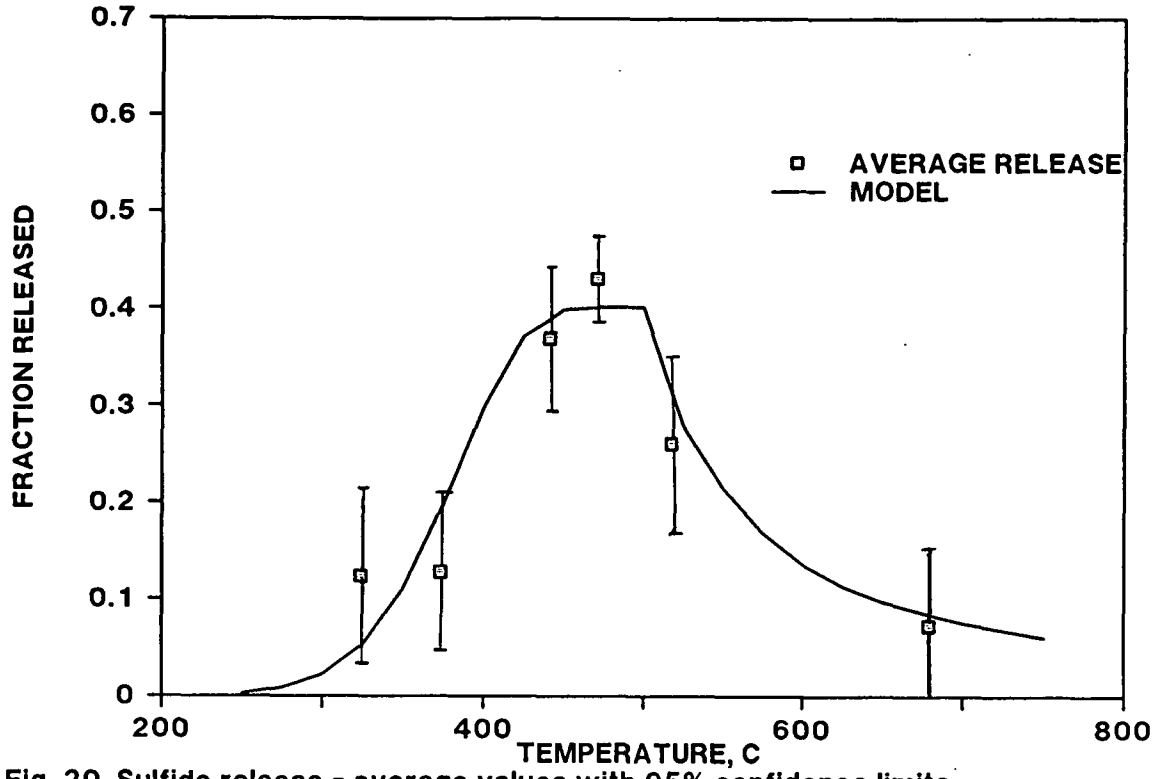

Fig. 20. Sulfide release - average values with 95% confidence limits; 9.0 seconds pyrolysis time.

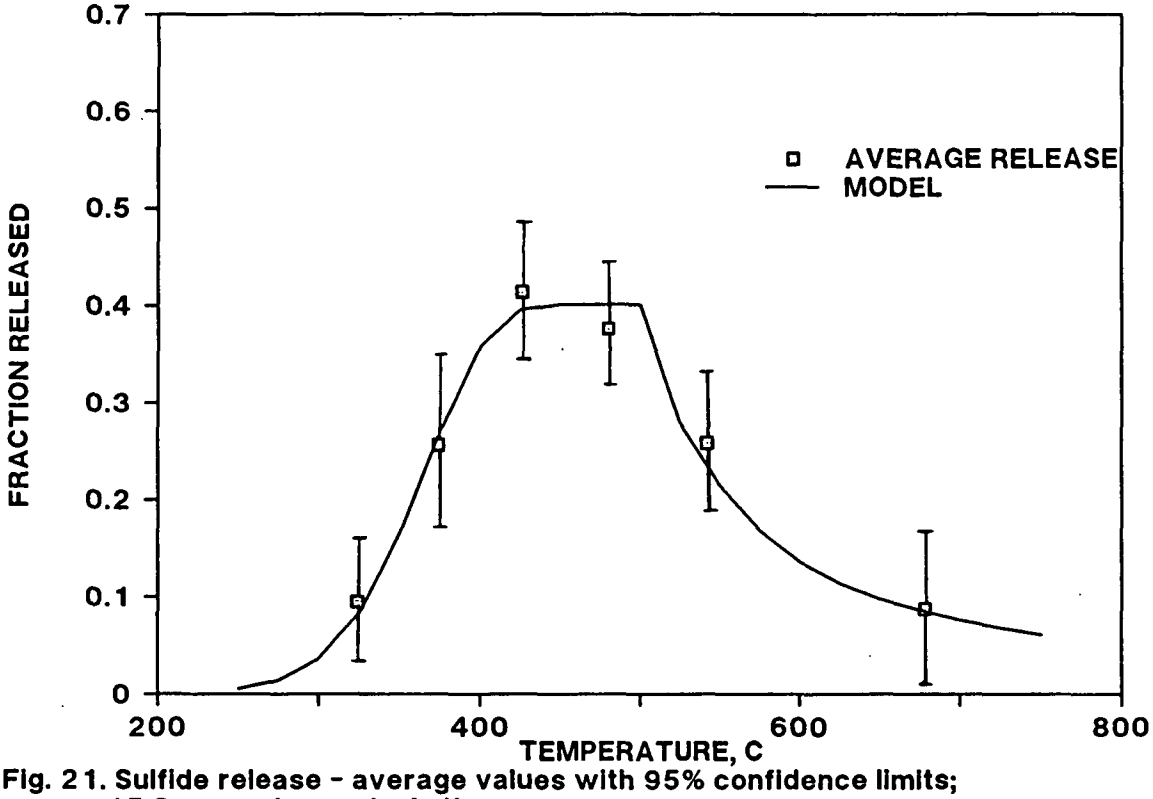

Fig. 21. Sulfide release - average values with 95% confidence limits; 15.0 seconds pyrolysis time.

As a measure of the error associated with the model, variances (s^2 values) were calculated from the residual sums of squares obtained in the lack-of-fit test described above. These variances reflect differences between the measured and predicted values that result both from the scatter in the data and from the model itself. For the thiosulfate model the s^2 value was 2.89×10^{-3}; for the sulfide model s^2 was equal to 7.87×10^{-3}. The corresponding s values are 0.054 for the thiosulfate model, 0.089 for the sulfide model.

Verification of Pyrolysis Kinetics Models

After the pyrolysis kinetics models for thiosulfate and sulfide were completed, tests were run to check the model's accuracy and to test for any interaction between thiosulfate and sulfide during pyrolysis that could affect the amount of sulfur released during black liquor pyrolysis. Two soda liquor samples to which solutions of sodium thiosulfate and sodium sulfide had been added were pyrolyzed using the pyrolysis kinetics reactor. The thiosulfate and sulfide contents of the liquors were determined using the modified Palmrose Iodate test and potentiometric titration with silver nitrate, respectively. The results of the pyrolysis tests and the amounts of sulfur predicted by the pyrolysis kinetics models are shown in Table 19. The results of the individual tests are shown in Table 29, Appendix 2. As can be seen by the results obtained, the model does a good job of predicting the amount of sulfur released by the liquors. Also, there is no evidence of interactions between thiosulfate and sulfide that would result in a modification of the amount of sulfur released during pyrolysis.

Table 19. Verification of pyrolysis kinetics model - soda liquors.
(Pyrolysis Time = 9.0 Seconds)

Liquor #	Thiosulfate Content (% as S)	Sulfide Content (% as S)	Average Temp. (°C)	Sulfur Released (mg S/100 g solids) Measured	Predicted
1	1.40	1.00	436	804 ± 63	844
2	1.41	0.98	431	806 ± 121	817

As an additional test, samples of four kraft liquors having various concentrations of sulfide and thiosulfate were pyrolyzed using the pyrolysis kinetics reactor. The results obtained from these tests were then compared to the amount of sulfur that would be expected to be released based on the analysis of the liquors. These comparisons are shown in Table 20. The complete results of the liquor analyses are shown in Table 21. Liquors number one and two were generated in pilot-scale cooks. Liquor number three is a liquor from a pilot scale cook to which additional sulfur (in the form of sulfide) was added. Liquor number four is a mill liquor.

Table 20. Verification of pyrolysis kinetics model - kraft liquors.
(Pyrolysis Time = 9.0 Seconds)

Liquor #	Thiosulfate Content (% as S)	Sulfide Content (% as S)	Average Temp. (°C)	Sulfur Released (mg S/100 g solids) Measured	Predicted
1	1.37	0.59	447	1092 ± 104	712
2	2.14	0.33	462	1001 ± 215	927
3	3.14	0.24	476	1448 ± 232	1248
4	0.80	2.08	429	1432 ± 128	1023

Table 21. Sulfur analysis of kraft black liquors.
All Values as Per Cent Sulfur

Liquor #	Content as SO_4^{2-}	SO_3^{2-}	$S_2O_3^{2-}$	S^{2-}	Sum of Col. 1-4	Total (Test)
1	0.50	0.40	1.37	0.59	2.86	3.35
2	0.37	0.24	2.14	0.33	3.08	3.37
3	0.33	0.24	3.14	0.24	3.87	4.33[a]
4	0.70	0.32	0.80	2.08	3.90	4.28[a]

[a] Total sulfur analyis by Huffman Laboratories, Golden, Colorado

The thiosulfate and sulfide models predict sulfur releases lower than those actually observed for all four kraft liquors. There are several possible explanations for the differences between the predicted and calculated values. First, although kraft and soda black liquors result from similar pulping processes, there are undoubtedly differences in the organic compounds present in the two types of liquor. It has been shown that the amount of sulfur released from inorganic sulfur compounds depends on the composition of the organic material with which the sulfur compounds are pyrolyzed[30,31]. Therefore, it is possible that the different organic composition of the kraft liquor allows an increased sulfur release.

Also, the pyrolysis model predicts sulfur release only from the sulfur present as sulfate, sulfite, thiosulfate, and sulfide. The kraft liquors contain, in addition to these four sulfur compounds, other sulfur species, as indicated by the difference in the total sulfur measured and the sum of the four sulfur compounds mentioned above (Table 21). These additional sulfur species, which are usually lumped under the category organic sulfur,

may also contribute to the sulfur release by kraft liquor. Although no concrete evidence for sulfur release from organic sulfur is known to exist, it is widely assumed that the sulfur contained in organic sulfur compounds is highly volatile[7,33]. Sulfur-carbon bonds are weaker than either carbon-carbon or carbon-oxygen bonds[64] and should therefore be more easily broken during pyrolysis. This organic sulfur is not accounted for by the model and could result in the increased sulfur volatilization observed from kraft liquor.

Finally, it can be noticed that the model predictions are further from the measured values for those liquors (1 and 4) that have larger fractions of their total sulfur present as sulfide. As was noted earlier, under certain circumstances, the sulfur release from sulfide can be considerably higher than the release predicted by the sulfur release model. Therefore, it is not surprising that sulfur release from liquors containing large amounts of sulfide will deviate further from predicted values than will the release from liquors whose volatile sulfur is chiefly present as thiosulfate.

HEAT TRANSFER MODEL

The heat transfer model simulates the temperature changes to and through a black liquor drop undergoing pyrolysis under nitrogen flow in the convective single particle reactor. The model is contained in the FORTRAN program BLTCAL and calculates the drop temperature at one-tenth second intervals for forty seconds. A copy of BLTCAL is included in Appendix 5.

The model program is divided into two parts. The first portion of the program reads the data file containing drop and reactor characteristics,

calculates the initial drop and gas flow parameters, and controls the drying of the drop. The inputs to the model include the nominal nitrogen flow to the reactor (cc/sec), the gas temperature, the wall temperature (both in ^{o}C), the drop's mass of solids (grams), solids content (fraction), and degree of swelling (cc/gram solids).

The drop is assumed to be spherical and is divided into three layers of equal mass. Using Cantrell's[22] equation for density as a function of solids content, the layers' dimensions are calculated. The volume and dimensions the drop will have after drying are also calculated. Following the results reported by Hupa et al.[12] and Clay et al.[21], it is assumed that the drop will swell to one and one-half times its original diameter during drying. Next, the variables that depend on the pyrolyzing gas's temperature and/or flow rate are calculated. These variables include the gas's specific heat and thermal conductivity, which are calculated as linear functions of temperature. A Nusselt number to be used in calculating convective heat transfer is also determined. It is calculated from:

$$Nu = 2.0 + 0.6\ Re^{1/2}Pr^{1/3} \tag{43}$$

Where Re and Pr are the Reynolds number and Prandtl number respectively.

After these preliminary calculations are done, drying parameters are calculated. The black liquor drop is assumed to enter the reactor at 100^{o} C and dry at a temperature of 150^{o} C. This temperature was reported by Hupa et al.[12] as being a typical drying temperature. The time required for drying is calculated from the drop's size, moisture content, and the amount of heat transferred to it by convection from the gas and radiation from the walls. At each one-tenth second interval, the total time the drop has spent

in the reactor is compared to the time required for drying. If drying is not complete, the drop's temperature is assumed to remain at 150°C. If sufficient time for drying has elapsed, the drying time is subtracted from the time spent in the reactor with this difference being passed to the second part of the program.

The second part of the program consists of a subroutine that controls pyrolysis of the black liquor drop. In this subroutine, the black liquor solid's properties are set or calculated, mass loss is determined, and black liquor swelling is handled. Finally, the temperature of the drop's layers are determined.

The first part of the subroutine sets several black liquor parameters including the heat capacity, thermal conductivity, and emissivity of the black liquor solids. As no independent data for the values of these parameters for black liquor solids at high temperatures are available, the values were determined by adjusting the specific heat and thermal conductivity of the black liquor solids until good fits between the predicted and actual values of temperatures were obtained. The value used for the black liquor solid's specific heat was 0.7 cal/g°C. A linear function of temperature was used to calculate the thermal conductivity. The equation used was

$$K_s = 5.0 \times 10^{-6} T - 2.0 \times 10^{-6} \quad (44)$$

with K_s the thermal conductivity (in cal/cm°C sec) and T the temperature (°C).

The mass loss during pyrolysis is also calculated. The total fraction of

mass that is lost by the drop during pyrolysis is determined by a linear function of the pyrolysis gas temperature. The mass loss totals 33% at a temperature of 500° C, and 45% at 900° C[65]. The rate of mass loss is an empirical function of the particle size, solids content, and pyrolysis gas temperature, and is based on the data of Clay and Ragland[62]. The mass-loss rate is:

$$B = (1.365 + .2065/R^2 - 4.0625S + 5.062T)\ M/100 \qquad (45)$$

where:

B = mass loss rate (fraction of total mass/second)

R = particle radius (cm)

S = solids content (fraction)

T = temperature (°C)

M = drop layer mass (grams).

A drop layer begins to lose mass due to pyrolysis when it reaches a temperature of 250° C.

The drop will swell during pyrolysis. The model assumes that the swelling begins when the drop layer's temperature reaches 250° C and is complete at a temperature of 500° C. The increase in volume is assumed to be linear with temperature. As the drop layers swell, the program calculates new volumes, layer densities, and thermal conductivities for the partially swollen layers. As the black liquor swells, gas pockets are formed within the drop. These pockets are assumed to be filled with a gas having thermal properties similar to nitrogen at the drop solids' temperature. The thermal conductivity of the swollen layer is calculated using Russell's equation[66] for thermal conductivity of porous solids:

$$K_c = K_s(K_g P^{2/3}/K_s + 1 - P^{2/3})/[K_g(P^{2/3} - P)/K_s + 1 - P^{2/3} + P] \quad (46)$$

where:

K_c = Thermal conductivity of composite

K_s = Thermal conductivity of solid

K_g = Thermal conductivity of gas

$P = (\rho_s - \rho_c)/(\rho_s - \rho_g)$

ρ_s = Density of solid

ρ_c = Density of the composite

ρ_g = Density of the gas

After the new drop dimensions and thermal parameters are calculated, the amount of heat transferred to each layer is determined and the temperature of the layers are calculated. The outer (surface) layer is heated by convection from the gas and radiation from the walls, and loses heat by conduction to the middle layer and by pyrolysis, which is assumed to be endothermic. The middle layer gains heat by conduction from the surface layer and loses it by conduction to the inner layer and through pyrolysis. The inner layer is heated by conduction from the middle layer and loses heat by pyrolysis. The equations describing the drop's heating are:

$$dT_s/dt = (Q_{cs} + Q_{rs} - Q_{ss} + Q_{ps})/(m_s C_{ps}) \quad (47)$$

$$dT_m/dt = (Q_{ss} - Q_{sm} + Q_{pm})/(m_m C_{pm}) \quad (48)$$

$$dT_i/dt = (Q_{sm} + Q_{pi})/(m_i C_{pi}) \quad (49)$$

with:

T = Temperature

t = time

m = mass of drop layer

C_p = Specific heat of black liquor solids

Q_{cs} = Heat convected to surface

$= \pi d^2 Nu\ K_g(T_g - T_s)/d$

Q_{rs} = Heat radiated to surface

$= \pi d^2 \epsilon F \sigma (T_r^4 - T_s^4)$

Q_{ss} = Heat conducted from surface

$= 4\pi K_{cm} r_s r_m (T_s - T_m)/(r_s - r_m)$

Q_{ps} = Heat lost to pyrolysis, surface layer

$= B_s H_p$

Q_{sm} = Heat conducted from middle layer

$= 4\pi K_{ci} r_m r_i (T_m - T_i)/(r_m - r_i)$

Q_{pm} = Heat lost to pyrolysis, middle layer

$= B_m H_p$

Q_{pi} = Heat lost to pyrolysis, inner layer

$= B_i H_p$

d = drop outer diameter

Nu = Nusselt number

K_g = Thermal conductivity of pyrolysis gas

ϵ = Emissivity of black liquor solids

F = View factor

σ = Stefan-Boltzmann constant

K_c = Thermal conductivity of swollen drop

r = Radius of drop layer

B = Mass loss rate

H_p = Heat of pyrolysis

Subscripts: s = surface layer

m = middle layer

i = inner layer

g = pyrolysis gas

r = radiant heat source.

These three differential equations are solved using a fifth and sixth order Runga-Kutta-Verner method to determine each layer's temperature as a function of time.

The heat transfer model was tested using several of the time-temperature histories obtained by pyrolyzing black liquor drops in the convective single particle reactor. Nine drops were chosen to use in matching the results of the model with those obtained experimentally. These drops were chosen to have a wide range of particle sizes and to include representatives from each solids/degree of swelling combination. Also, only drops whose initial measured temperature was at or below 100^{o} C were selected. This criterion was imposed to insure that the drop's entire drying history was included in the collected temperature measurements. The heat transfer model program was run using the selected drop's size, solids content, the average degree of swelling for the liquor from which the drop was made, and the single particle reactor's operating conditions as inputs. The heating profiles thus obtained were compared to the experimentally obtained results and modifications were made to the model's black liquor parameters to improve the fit. The models were then rerun and the newly obtained results compared to the experimental values. This procedure was repeated until further adjustments were deemed unproductive. The drops' experimental temperature profiles and those obtained from the model are shown in Figs. 22 - 30.

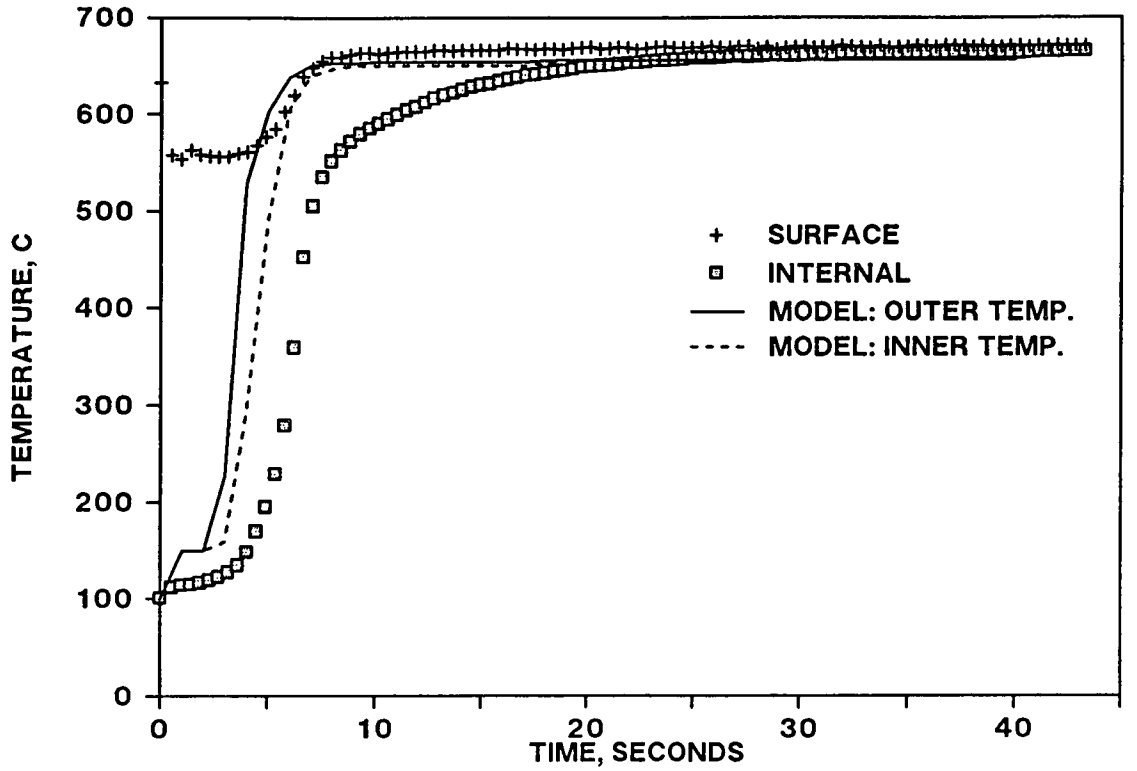

Fig. 22. Black liquor pyrolysis temperature model - test #138; 6.4 mg drop; 62.7% solids; 55.5 cc/g swelling.

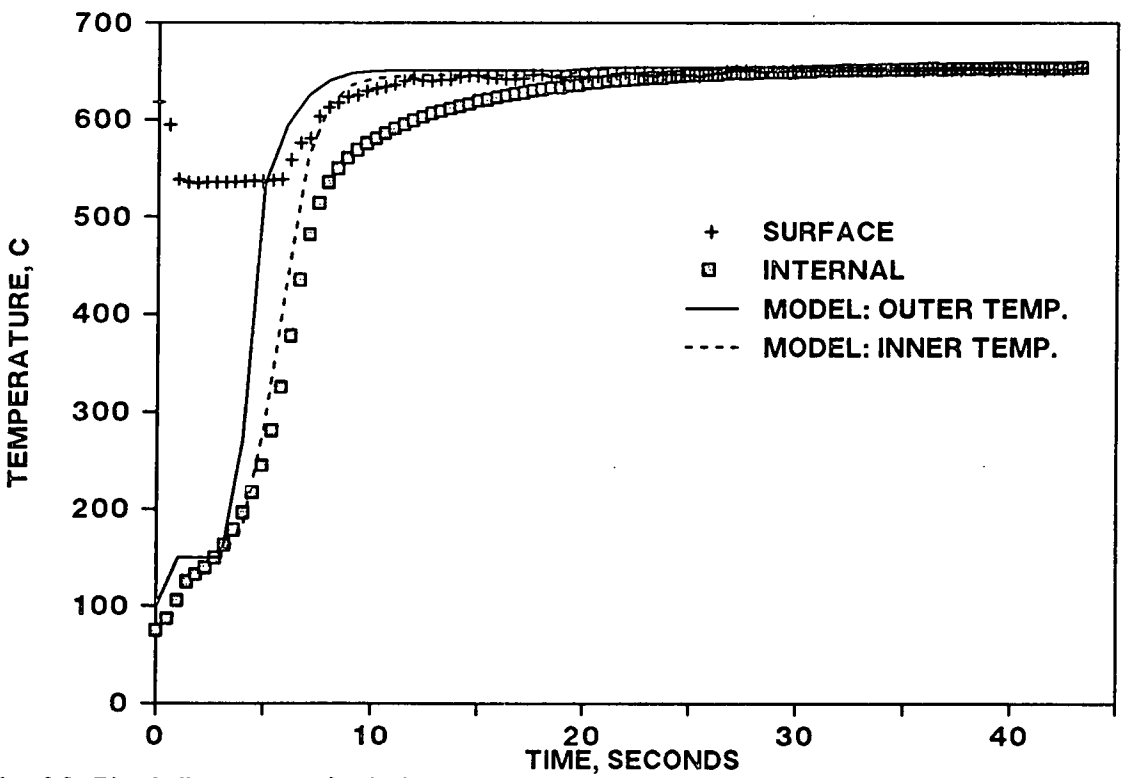

Fig. 23. Black liquor pyrolysis temperature model - test #145; 10.3 mg drop; 62.7% solids; 55.5 cc/g swelling.

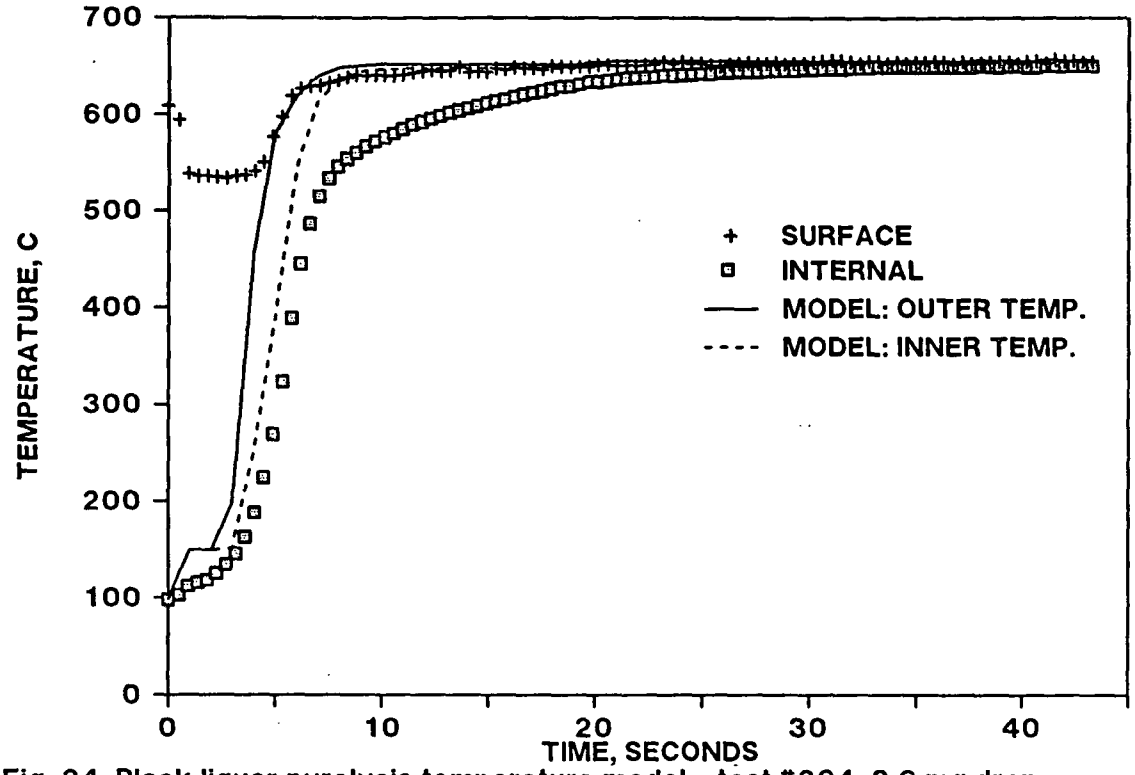

Fig. 24. Black liquor pyrolysis temperature model - test #204; 8.6 mg drop; 66.9% solids; 51.7 cc/g swelling.

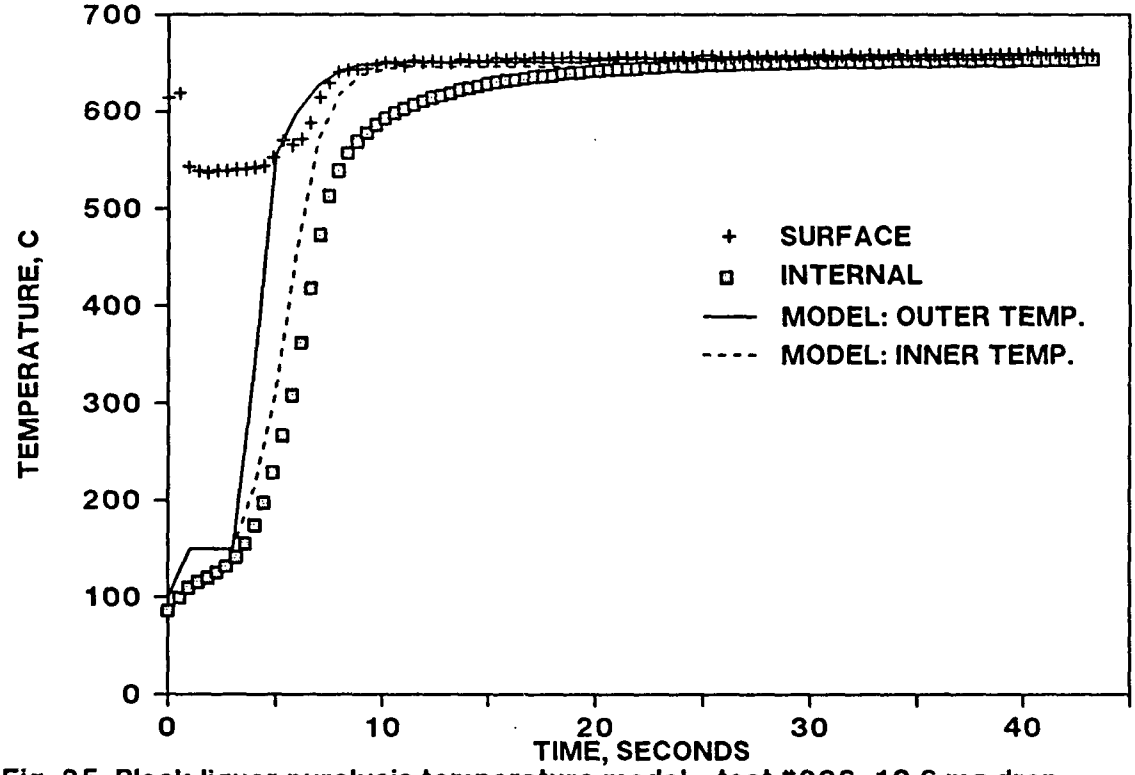

Fig. 25. Black liquor pyrolysis temperature model - test #206; 10.6 mg drop; 66.9% solids; 51.7 cc/g swelling.

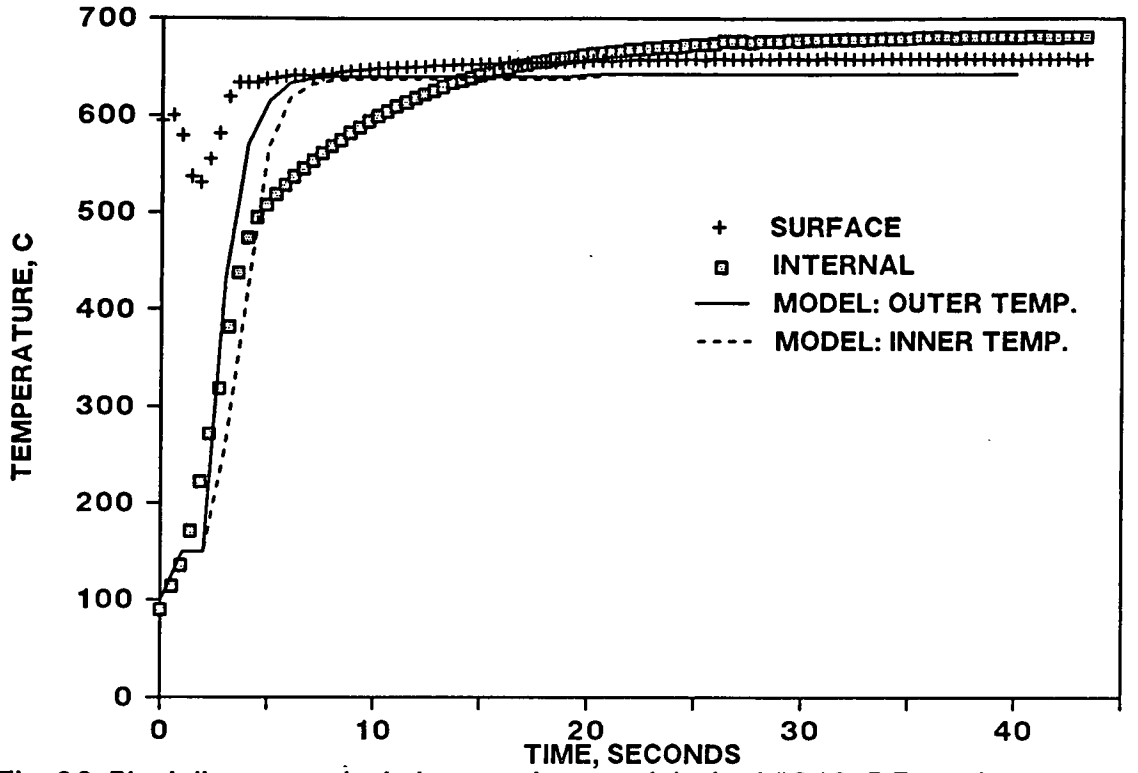

Fig. 26. Black liquor pyrolysis temperature model - test #310; 5.7 mg drop; 74.0% solids; 46.0 cc/g swelling.

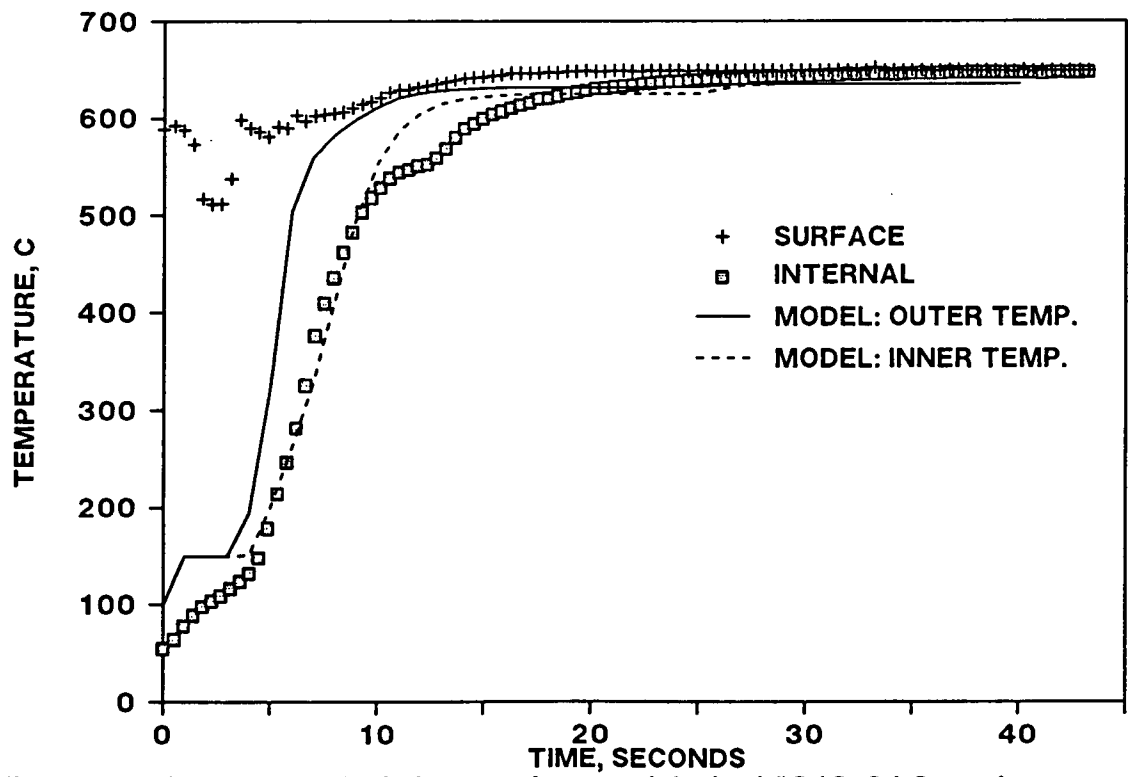

Fig. 27. Black liquor pyrolysis temperature model - test #313; 21.8 mg drop; 74.0% solids; 46.0 cc/g swelling.

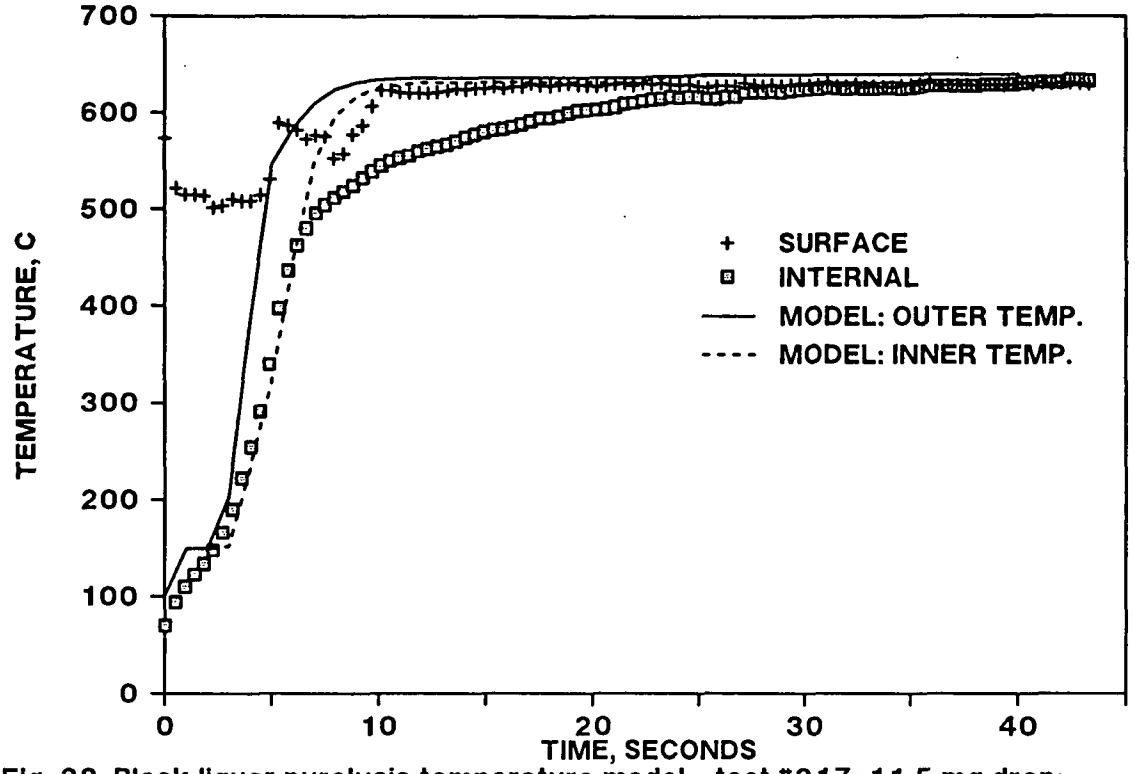

Fig. 28. Black liquor pyrolysis temperature model - test #317; 11.5 mg drop; 74.0% solids; 46.0 cc/g swelling.

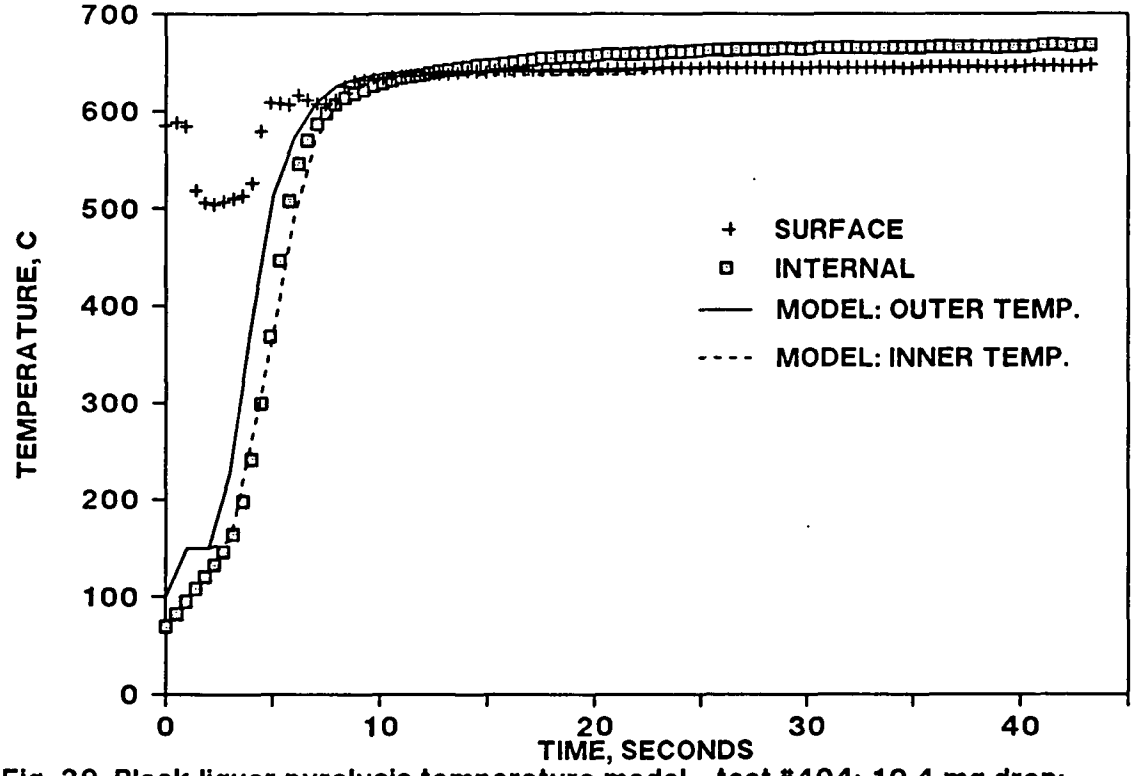

Fig. 29. Black liquor pyrolysis temperature model - test #404; 10.4 mg drop; 74.0% solids; 23.8 cc/g swelling.

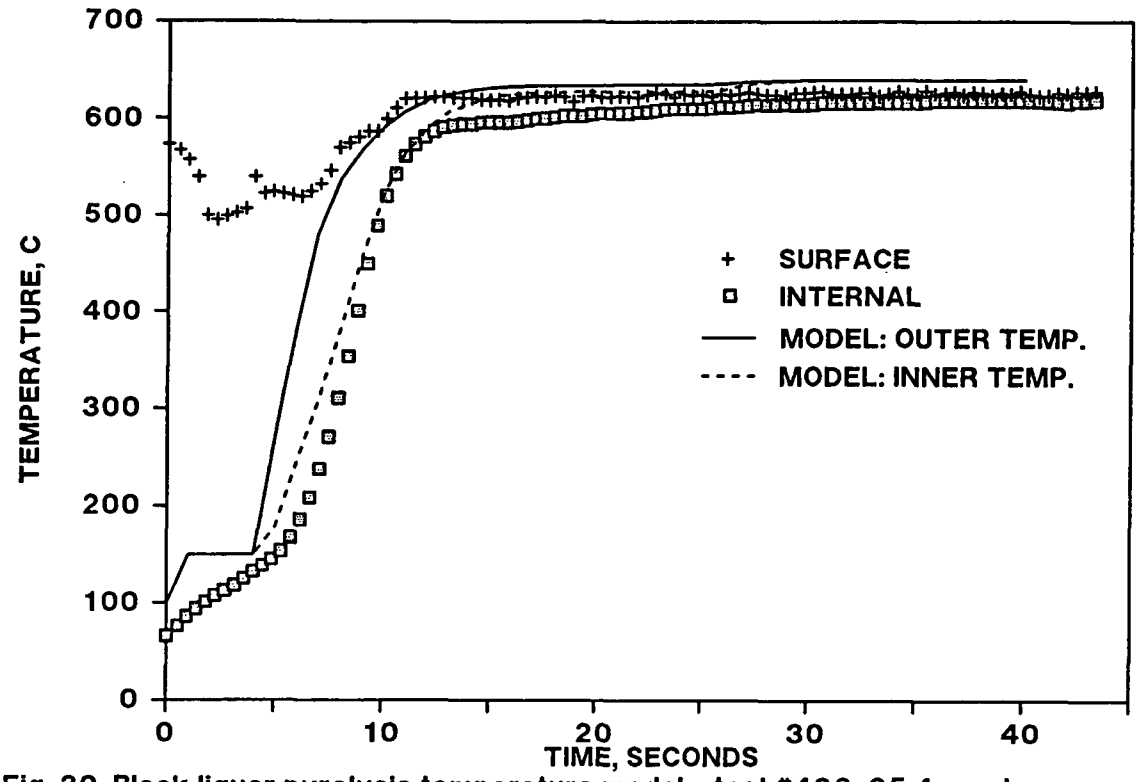

Fig. 30. Black liquor pyrolysis temperature model - test #406; 25.4 mg drop; 74.0% solids; 23.8 cc/g swelling.

The model predictions shown in Figs. 22 - 30 best match the experimental values for the external and internal temperatures of Runs 404 and 406. These drops were made from liquor to which a swelling retardant had been added. It is believed that the difference in swelling between these and the other drops, at least in part, accounts for the differences observed between the measured and predicted temperature profiles.

Cross sections of pyrolyzed drops exhibiting good and poor swelling characteristics are shown if Figs. 31 and 32. From the Figs. it can be seen

that the internal structures of the two drops are quite different. The drop having good swelling characteristics consists of a outer shell of char surrounding a hollow center. The poor swelling drop, on the other hand, has a denser and more uniform particle interior. Thus, during pyrolysis, the thermocouple inside the poor swelling drop will be heated mainly by conduction through the pyrolyzing char, while the thermocouple inside the good swelling drop will be heated less by conduction and more by radiation from the inside surface of the drop's outer shell. As the particle continues to swell the thermocouple may become entirely deattached from the pyrolyzing char. In this situation, the thermocouple will reflect the temperature of the gas inside the pyrolyzing particle instead of the temperature of the particle's solids.

OVERALL DROP MODEL

The pyrolysis kinetics model and the heat transfer model were combined to produce an overall model that predicts the amount of sulfur released during the pyrolysis of a black liquor drop as a function of the drop's size, solids content, degree of swelling, and sulfur content, as well as the temperatures and gas flow to which the black liquor particle is subjected.

The overall drop model is contained in the computer program SULREL, found in Appendix 6. This model follows the same calculation scheme found in the heat transfer modeling program with the following exceptions.

First, in order to make the model applicable to reactor systems other than the convective single particle reactor, the gas flow is input as a gas velocity rather than a volumetric flow. Second, the differential equations

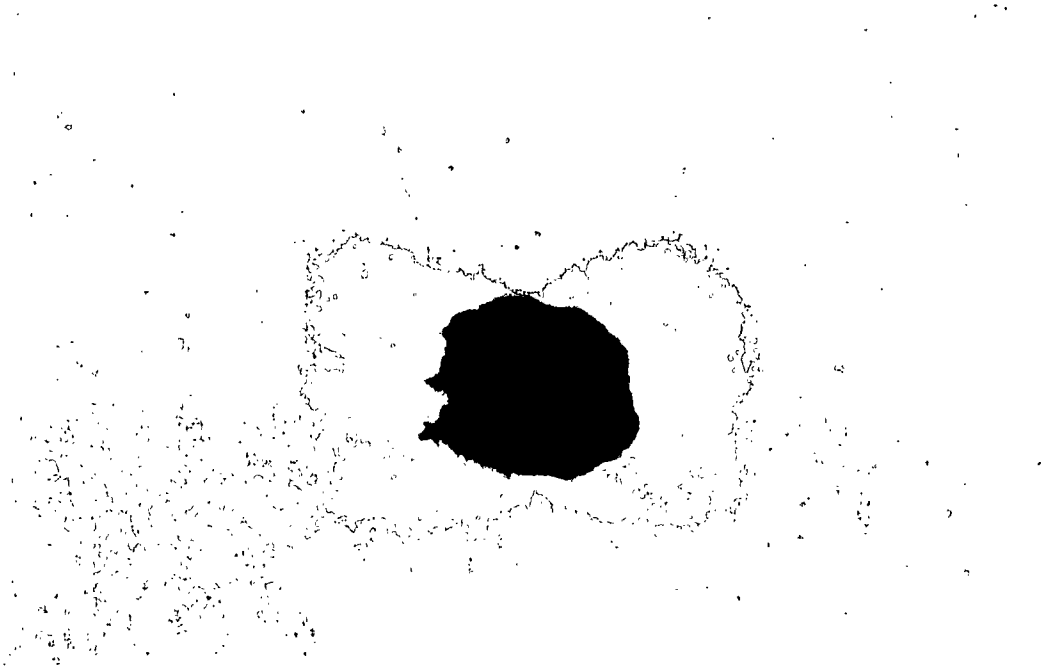

Fig. 31. Black liquor drop exhibiting normal swelling.

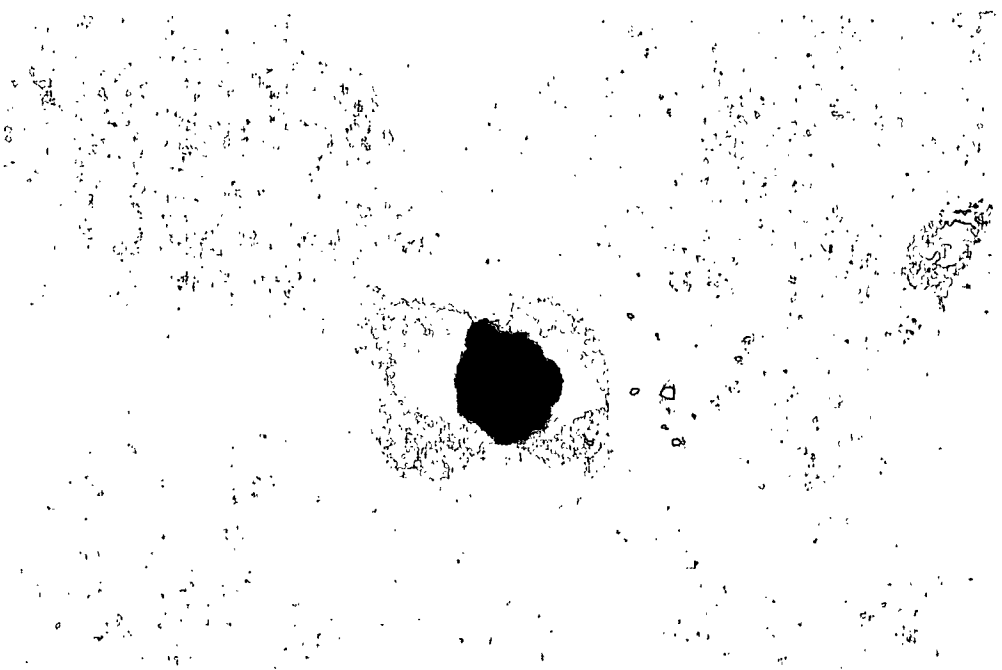

Fig. 32. Black liquor drop exhibiting reduced swelling.

that describe sulfur release kinetics are included in the model. These equations have the form:

$$dS/dt = K_0 \exp(-E/RT)(FS^* - S) \quad (50)$$

with:

S = concentration of the volatile sulfur species (thiosulfate or sulfide)

t = time

K_0 = pre-exponential factor

E = activation energy

R = gas constant

T = absolute temperature

F = empirical factor

= exp(A/T + B); A, B = constants

S^* = maximum amount of sulfur that can be released.

The program solves the two sulfur release equations (one for thiosulfate, the other for sulfide) and the heat transfer equation which calculates the temperature of the drop layer.

VERIFICATION OF OVERALL DROP MODEL

After the overall drop model was completed, its results were compared to the results from the tests which determined the effect of drop size, solids content, and degree of swelling. The average drop size, liquor solids content, and degree of swelling for each of the three liquors, the liquors' thiosulfate and sulfide concentrations, as well as the temperature and gas velocity at which the test were conducted were used as inputs to the model. Table 22 shows the results of the model predictions compared to the measured

sulfur releases.

For every case tested, the sulfur release predicted by the model is lower than the amount measured during the experimental runs. Part of the discrepency between the calculated and observed values is probably due to the differences between soda test liquors used to develop the model and a kraft liquor. These differences include a difference in organic composition and the presence of additional volatile sulfur species in the kraft liquor. These factors are discussed above in the section titled "Verification of Pyrolysis Kinetics Models".

Table 22. Comparison of actual and predicted sulfur releases from drops of different weights and solids contents. Pyrolysis temperature = 665° C

Solids (%)	Drop Weight (mg solids)	Sulfur Release (mg S/100 g solids) Actual	Predicted
63.4	6.5	546	422
	12.6	541	449
	24.7	810	489
77.7	7.9	608	437
	14.9	754	471
	30.7	891	519
76.7	7.9	643	461
	14.9	731	499
	29.4	874	547

In addition to lower overall sulfur releases predicted, the model also underpredicts the effect that changing the drop size or solids content will have on the amount of sulfur volatilized during pyrolysis. A possible explanation for difference between predicted and measured sulfur releases is that a chemical reaction, such as oxidation of the sulfide, that lowered the

amount of sulfur released, took place on the surface of the drop between the time the drops were prepared and when they were pyrolyzed. As the smaller drops had a larger surface area to mass ratio than did the larger drops, any surface reaction that affects sulfur release would have a larger impact on the smaller drops. This reaction would have had an even bigger impact on liquor pyrolyzed as a thin film, as was the case during the development of the pyrolysis models, as essentially all the liquor will be exposed to air during the sample preparation.

This explanation, however, is unlikely to account for the differences observed between the predicted and measured sulfur releases. First, had the sulfide in the liquor used to generate the pyrolysis model oxidized during sample preparation, the results of the sulfide and thiosulfate pyrolysis experiments should have been very similar. In fact, as can be seen from Figs. 6 - 9 and 11 - 13 and from the values of the two models' constants, the results of experiments involving pyrolysis of thiosulfate-containing liquor are very different from those which pyrolyzed liquor containing sulfide. Also, the kraft liquor used in the experiments to determine the effects of drop size, solids content, and degree of swelling, had most of its sulfur present as thiosulfate. Thus, even if some oxidation had occured, it would be unlikely to result in as large an impact as is shown in the experimental results.

A more likely explanation for the increased sulfur release seen during pyrolysis of larger drops is the increased opportunity for reaction between the liquor's sulfur compounds and pyrolysis products that results in formation of sulfur-containing gases. Many of the proposed sulfur release

reaction mechanisms show sulfur-containing gases resulting from reaction of inorganic sulfur compounds with pyrolysis products (such as CO_2 and H_2O). When the liquor is pyrolyzed as a thin film, as was the case during the pyrolysis experiments, there is limited opportunity for contact between the pyrolysis products and the sulfur compounds. When the liquor is pyrolyzed in the form of a drop, on the other hand, there is a chance for the pyrolysis products escaping from the drop's interior to react with sulfur compounds in the drops outer regions, resulting in the production of sulfur-containing gases. Larger drops will present pyrolysis gas products with longer pathways from their place of formation to the drop's surface and thus provide greater opportunity for them to encounter and react with sulfur compounds.

Increased opportunity for interaction between sulfur species and pyrolysis products may also be responsible for the increased sulfur release observed during pyrolysis of high-solids liquors relative to those with lower solids levels. It has been observed by Miller[13] and in the present study that increasing a liquor's solids content will result in a decrease in the amount of swelling the liquor undergoes during pyrolysis. This decrease in swelling will result in a denser pyrolyzing drop which could provide additional contact between escaping pyrolysis products and sulfur compounds present in the partially pyrolyzed char.

Another factor that could account for some of the differences observed in sulfur release between liquors of different solids contents is the amount of swelling that takes place during drying. In addition to having lower amounts of swelling during pyrolysis, it has also been observed that higher solids liquors tend to swell less during drying than do liquors having lower

solids contents[67]. Since the model assumes that all liquors swell equally during drying, regardless of solids content, any increase in drop size during drying by a low solids drop above that attained by a high solids drop will not be reflected in the model's heat transfer calculations.

The additional opportunity for contact and reaction between pyrolysis products and liquor sulfur compounds may also account for the increased sulfur release observed by Feuerstein[29] and Jones[17] over that seen in the present study. In the pyrolysis study conducted by Feuerstein, the black liquor was pyrolyzed in large quantities (100 ml of 65% solids liquor) inside a bomb-type reaction vessel. This experimental setup resulted in the liquor being pyrolyzed as a single mass (in essence a very large drop), which provided ample opportunity for reaction between pyrolysis products and the sulfur present. The experimental apparatus used by Jones injected fresh liquor into the reaction vessel throughout the test, thus providing a continuous supply of pyrolysis products to react with the sulfur present in the pyrolyzing liquor and char. Therefore, because of the increased opportunity for reaction between the sulfur contained in the liquor and the pyrolysis products, a higher sulfur release than that observed by the present study would be possible.

SUMMARY

A model has been developed to describe sulfur release from a black liquor drop undergoing pyrolysis. This model predicts the amount of sulfur volatilized as a function of the concentration of the various sulfur species contained in the black liquor, the drop's size, solids content, and swelling characteristics, and the heating environment to which the drop is exposed.

The model employs a modified first order decomposition model to predict the amount of sulfur released by sodium thiosulfate and sodium sulfide. The maximum amount of sulfur that can be released at any temperature is controlled by an empirically derived factor that decreases with increasing temperature. About forty per cent of the sulfur contained in sodium thiosulfate can be volatilized during black liquor pyrolysis. The amount of sulfur that can be released from thiosulfate is a maximum at temperatures around four-hundred eighty degrees C. The sodium sulfide contained in the black liquor can also release up to forty per cent of its sulfur during pyrolysis. Sulfur release from sulfide begins to decline above temperatures of about four-hundred ninety degrees. Sodium sulfate and sodium sulfite are modeled as being non-volatile as the amount of sulfur released from these compounds is small.

The results obtained in this study for the maximum amounts of sulfur that can be released from thiosulfate or sulfite are similar to the values reported by Douglas and Price[28] during pyrolysis of inorganic sulfur species with soda lignin. Douglas and Price found that thirty-seven to thirty-eight per cent of the sulfur contained in either sulfur compound volatilized during pyrolysis with soda lignin.

The model also calculates the temperature of a black liquor drop undergoing pyrolysis as a function of the liquor particle's physical characteristics and the heating environment to which the drop is exposed. This temperature is then used in the kinetic models described above to predict the total amount of sulfur released from the drop. Any changes in black liquor characteristics that slow the heating rate, such as increasing drop size or solids content, or decreasing the amount of swelling that the drop undergoes during pyrolysis, result in increasing the amount of sulfur volatilized.

CONCLUSIONS

1. The amounts of sulfur that are volatilized from various sulfur species contained in kraft black liquor have been determined as functions of time and temperature. Sodium sulfide can release up to forty per cent of its sulfur during pyrolysis. This maximum release can be obtained at temperatures of up to 490° C. At higher pyrolysis temperatures, the maximum sulfur release decreases with increasing temperature. Sodium thiosulfate also releases up to forty per cent of its sulfur during pyrolysis. This maximum release is possible at or below temperatures of 480° C; at higher temperatures the amount that can be released declines. The rate of release from thiosulfate is lower than the sulfide release rate. Sodium sulfate releases only small amounts (1% or less) of sulfur during pyrolysis. Sodium sulfite also release only minor amounts (2%) of sulfur when undergoing pyrolysis. Organic sulfur is volatile under pyrolysis conditions. However, because of the small amounts of organic sulfur contained in the test sample and the wide variation in the test results, no conclusions about the amount of sulfur that can be released from organic sulfur can be drawn.

2. Increasing drop size increases the amount of sulfur that is volatilized from a pyrolyzing black liquor drop. Increasing the liquor's solids content results in an increase in the amount of sulfur released by the drop. Decreasing the liquor's swelling by addition of a swelling retardant increases the amount of sulfur released from a drop during pyrolysis. The amount of increase that is observed will depend on the liquor's sulfur composition and the environment in which it is pyrolyzed.

3. A model describing sulfur release from a pyrolyzing black liquor drop

has been developed. This model uses external heat transfer to determine the drop temperature. The drop temperature is then used in kinetic models that calculate sulfur release from thiosulfate and sulfide.

4. The model developed indicates that the sulfur release rate is at a maximum when the liquor temperature is in the 350 - 550^{o} C range. Therefore, any change in recovery boiler operation that minimizes the length of time liquor particles are at these temperatures will reduce the amount of sulfur volatilized. Changes that could result in lower sulfur release include increasing lower furnace temperature and adjusting spray distribution so that the liquor pyrolyzes in the hottest section of the furnace. Oxidation of the black liquor may also reduce the amount of sulfur volatilized during pyrolysis, if the liquor is rapidly heated to temperatures above those where sulfur release occurs.

IMPLICATIONS FOR RECOVERY BOILER OPERATION

EFFECT OF BLACK LIQUOR OXIDATION ON SULFUR RELEASE

The results of the present work show that similar amounts of sulfur can be released from either sodium sulfide or sodium thiosulfate during pyrolysis of kraft black liquor. However, the rate of release from sulfide is much greater than the thiosulfate release rate. Therefore, a black liquor drop whose sulfur content is chiefly thiosulfate, as a result of black liquor oxidation, may release less sulfur during pyrolysis than will a similar drop whose sulfur content is mainly in the form of sulfide, especially if the drop is rapidly heated through the temperatures at which sulfur volatilization is at a maximum. Tests of the overall drop model on black liquor drops having similar size, solids, and swelling characteristics, but whose sulfur content is composed entirely of single sulfur compound (thiosulfate or sulfide) have given significantly different results. About 20% less sulfur is released from a drop whose sulfur is present as thiosulfate than from a similar drop whose sulfur is present as sulfide. This reduced sulfur release could result in additional benefits for the boiler, as the amount of fuming required to react with the sulfur will decrease. A decrease in generated fume will reduce the particulate loading in the gas passages of the boiler's convective heat transfer section.

It should be emphasized, however, that the benefit of reduced sulfur release can only be realized if the oxidized liquor is heated rapidly so as to spend a minimum amount of time at temperatures where sulfur release is at a maximum.

Black liquor oxidation affects other liquor properties in addition to

converting the sulfide to thiosulfate. Perhaps the most important of these changes in liquor properties is in an increase in liquor viscosity due to the lowering of the liquor's alkali level. Changing the liquor's viscosity may result in an altered drop-size distribution when the liquor is fired inside the boiler. Changing the distribution of drop sizes produced during spraying will affect the amount of sulfur that is released during pyrolysis or burning. The impact on drop-size distribution due to viscosity changes could, however, be offset by an appropriate change in the liquor's temperature.

Black liquor oxidation also lowers the liquor's fuel value and offers the possibility of increased liquor solids throughput at the same steaming rate. One such patent proposes this concept[68]. In this process, part of the black liquor generated by the pulping operation be oxidized to on extent that its heating value is substantially reduced. This oxidized liquor is then mixed with the remaining, unoxidized, liquor to form a black liquor with a lower fuel value. This decrease in liquor heating value allows an increase in boiler firing capacity.

USE OF ELEMENTAL SULFUR AS A MAKEUP CHEMICAL

Many mills use elemental sulfur as a makeup chemical to replace sulfur lost by the liquor during the pulping and recovery cycle. This sulfur, usually in the form of a high-solids emulsion, is added to the black liquor just prior to firing it into the recovery furnace. Date and Hight[69] claim that this method of adding sulfur to the liquor, rather than the traditional one of adding saltcake (sodium sulfate), results in several advantages. Among these benefits are easier handling and mixing of makeup chemical, an increased

furnace efficiency, as the elemental sulfur does not have to be reduced, lower lime usage, and lower sulfur release because of a hotter furnace temperature and increased generation of fume. The lower sulfur release results in less plugging of the boiler's air passages as the generation of sulfur-containing sticky deposits is lowered.

However, Nelson[70] claims that adding elemental sulfur to the black liquor increases the amount of sulfur released during burning. This sulfur, in the form of SO_2, is said to result in increased corrosion and fouling as the sulfur dioxide is absorbed by ash deposits on the convective heat transfer surfaces.

In addition to the possibility of being burned to SO_2 in the recovery furnace, elemental sulfur can react with the sodium hydroxide contained in black liquor to form sodium sulfide and sodium thiosulfate according to the reaction:

$$4S + 6NaOH \Rightarrow 2Na_2S + Na_2S_2O_3 + 3H_2O^{71} \qquad (52)$$

Both of these products can release large amounts of sulfur during black liquor pyrolysis. Sodium sulfate, on the other hand, is essentially stable with respect to sulfur release during pyrolysis. Although the burning temperature of the liquor should increase with use of elemental sulfur as a makeup chemical, due to its fuel value and the fact that it does not need to undergo an endothermic reduction reaction, this increase in combustion temperature is likely to be small. Thus, it seems probable that the addition of elemental sulfur to kraft black liquor as a makeup chemical, instead of saltcake, will result in increased sulfur volatiliztions during black liquor combustion.

RECOMMENDATIONS

Additional research is recommended in two areas: determining the causes of the increase in sulfur release due to increasing size and solids content, and; extension of the study of compositional variables to burning drops.

The present study has shown that heat transfer effects, by themselves, do not account completely for the increase in sulfur release observed when particle size or solids content is increased. It is suspected that this increase may be the result of reaction of sulfur species contained in the outer portions of the drop with pyrolysis products being released from the particle's inner regions. Quanitifying the production of other pyrolysis products, especially CO_2 and H_2O, which have been suggested as reactants in sulfur release reactions, would aid in determining the reasons for the enhanced sulfur release seen when particle size or solids content is increased.

Sulfur release during pyrolysis is greatly affected by the compounds in which the sulfur is present and by the physical characteristics of the drop, such as size and solids content. However, pyrolysis is only one of the stages of burning that a black liquor drop goes through during combustion in a recovery boiler. Study of the effect of the compositional and physical variables during burning in oxygen containing atmospheres will provide additional insight into the release of sulfur in recovery boilers.

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APPENDIX 1: LIQUOR ANALYSIS AND PREPARATION

Modified Palmrose Iodate Titration

The black liquor sample, equivalent to 0.3 - 0.5 grams of solids, is dissolved of water. If sulfides are present in the liquor, they are removed by mixing the black liquor sample with a one normal zinc carbonate suspension that is prepared by mixing ten milliliters of one normal sodium carbonate with ten milliliters of one normal zinc sulfate. The liquor is then filtered and a 25.0 milliliter sample of the filtrate mixed with ten milliliters of one normal sulfuric acid and two ml of 1.5 normal potassium iodide. The solution is then titrated with 0.025 N potassium iodate using a starch indicator. The results of this titration indicate the amount of sulfur present as sulfite and thiosulfate.

Prepartion of Liquor Containing Only Organic Sulfur

To prepare a liquor containing only organic sulfur, it was necessary to remove the ionic sulfur species from the kraft black liquor. A sample of kraft liquor was diluted to approximately fifteen per cent solids. Carbon dioxide was then bubbled through the liquor to precipitate the lignin. The liquor was then centrifuged and the supernatant decanted. The lignin was then transferred to an electrodialysis cell and electrodialysis was used to remove the charged species from the lignin. The lignin was then mixed with the supernatant from a sample of soda liquor whose lignin had also been precipitated with carbon dioxide. Sodium hydroxide was then added to the mixture to redissolve the lignin and the liquor was concentrated by rotary vacuum distillation.

APPENDIX 2: RESULTS OF PYROLYSIS EXPERIMENTS

Below are listed the results of the individual experiments used to formulate the pyrolysis kinetics models.

Table 23. Pyrolysis of sulfate-containing soda liquor.

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	428	0
	452	0
	440	0
	458	0
	452	0
	431	0
	434	19
	452	0
	446	7
	440	0
10.5	464	22
	458	6
	437	3
	472	0
	422	0
	446	0
	440	0
	422	4
	458	11
	461	8
15.0	452	17
	434	10
	434	0
	446	1
	464	0
	434	0
	470	11
	476	34
	431	7
	476	0

Table 23. Pyrolysis of sulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	731	10
	737	0
	779	11
	743	15
	749	10
	743	7
	767	22
	758	21
	725	9
	761	0
10.5	749	15
	743	18
	761	15
	713	32
	737	18
	731	0
	749	27
	728	0
	758	30
	749	10
15.0	761	32
	731	71
	743	54
	755	14
	749	10
	761	16
	722	34
	725	29
	773	25
	731	16

Table 24: Pyrolysis of sulfite-containing soda liquor.

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	446	42
	452	27
	428	54
	437	62
	428	25
	425	55
	464	59
	446	46
	440	60
	440	11
10.5	452	22
	434	24
	452	25
	410	0
	428	40
	437	36
	458	76
	434	93
	434	15
	479	29
15.0	458	14
	461	23
	443	84
	428	0
	428	129
	434	29
	455	45
	440	107
	476	71
	440	73

Table 24. Pyrolysis of sulfite-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	719	74
	696	33
	678	42
	743	56
	702	0
	678	0
	725	20
	704	52
	743	27
	702	20
10.5	719	52
	725	18
	693	56
	684	30
	737	61
	719	93
	684	7
	725	11
	702	45
	684	22
15.0	719	22
	734	0
	702	70
	719	13
	681	64
	681	26
	725	34
	707	73
	696	57
	731	95

Table 25. Pyrolysis of thiosulfate-containing soda liquor.

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	276	37
	268	70
	268	41
	256	89
	256	0
	288	230
	297	342
	268	103
	294	222
	273	280
10.5	279	233
	285	396
	262	326
	256	233
	291	451
	256	178
	291	260
	268	147
	297	7
	288	102
15.0	256	49
	262	252
	297	195
	279	185
	276	308
	268	176
	268	240
	279	315
	273	346
	297	601

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	333	553
	315	199
	297	301
	345	768
	327	405
	321	287
	363	291
	336	118
	333	240
	303	148
10.5	315	236
	321	222
	333	599
	354	388
	324	703
	312	508
	339	128
	309	586
	327	417
	321	370
15.0	333	247
	321	573
	345	642
	339	731
	318	573
	315	491
	333	702
	342	717
	321	477
	318	627

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
9.0	440	996
	422	909
	458	959
	431	960
	422	946
	434	1059
	452	864
	434	918
	461	945
	434	851
	452	808
	428	1007
	428	1000
	428	840

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	422	470
	440	709
	428	705
	452	714
	464	1132
	470	720
	422	1125
	440	1206
	458	1130
	482	854
10.5	455	815
	452	1076
	452	1010
	440	910
	455	1074
	428	1122
	452	1265
	434	1134
	476	1447
	470	939
15.0	431	1365
	470	1234
	428	1074
	434	1165
	464	1485
	458	1511
	446	1267
	455	1455
	473	1099
	470	1371

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	547	763
	547	514
	559	435
	562	557
	550	620
	577	676
	541	496
	577	654
	553	353
	565	1048
10.5	547	851
	547	595
	571	570
	553	707
	553	502
	559	804
	553	650
	557	1015
	553	735
	553	760
15.0	565	752
	556	625
	559	621
	565	476
	571	834
	562	1074
	565	664
	556	737
	574	893
	556	764

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
10.5	755	190
	707	230
	743	402
	731	439
	737	553
	737	603
	731	550
	752	183
	749	445
	699	376
15.0	719	390
	734	445
	719	366
	731	430
	755	489
	734	374
	734	483
	725	335
	719	166
	755	440

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
9.0	571	621
	577	859
	547	900
	556	942
	523	1154
	538	1201
	523	952
	538	1122
4.5	583	678
	565	709
	592	669
	571	901
	586	726
	583	595
	568	793
9.0	571	770
	565	801
	586	727
	577	1027
	583	777
	577	968
	589	1027

Table 25. Pyrolysis of thiosulfate-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	511	838
	526	952
	529	871
	529	825
	493	808
	499	824
	505	793
9.0	523	1113
	505	911
	523	914
	517	1310
	493	1081
	493	1091
	517	964

Table 26. Pyrolysis of sulfide-containing soda liquor.

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	307	71
	348	170
	296	32
	293	68
	303	313
	346	283
	337	50
9.0	336	366
	354	167
	307	138
	310	243
	366	146
	313	417
	338	267
15.0	303	315
	318	213
	327	237
	351	409
	338	299
	314	201
	354	425

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	379	248
	401	381
	369	275
	388	312
	417	320
	354	445
	353	364
9.0	375	297
	341	504
	359	545
	414	624
	376	593
	388	706
	396	470
15.0	396	908
	434	809
	403	551
	437	1242
	382	1105
	348	489
	389	583

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	432	1191
	434	685
	420	1182
	462	1213
	467	680
	474	692
	426	673
9.0	444	883
	448	1067
	438	840
	443	550
	495	1614
	452	893
	454	1132
15.0	416	957
	444	1350
	404	1271
	429	979
	433	1480
	433	839
	479	783

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	526	728
	539	539
	495	642
	528	442
	545	658
	532	695
	546	611
9.0	482	734
	499	1021
	506	893
	522	429
	503	766
	531	588
	528	847
15.0	529	669
	477	607
	533	482
	571	749
	531	884
	552	493
	538	859

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	660	313
	681	297
	693	162
	699	215
	678	400
	692	264
	685	247
9.0	701	256
	676	226
	672	369
	674	182
	669	173
	688	233
	676	178
15.0	713	184
	682	244
	676	208
	672	304
	659	350
	670	292
	672	260

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
4.5	488	998
	486	817
	456	946
	483	864
	459	1008
	436	1214
	441	918
9.0	446	1132
	466	1125
	472	1011
	462	1038
	479	1148
	469	1243
	459	1191
15.0	485	1005
	463	865
	472	1027
	461	1057
	485	1224
	456	1159
	460	1179

Table 26. Pyrolysis of sulfide-containing soda liquor (Continued).

Time (sec)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
9.0	446	762
	485	863
	474	947
	454	1112
	470	1130
	449	1668
	460	1120

Table 27. Lack-of-fit analysis, thiosulfate model.

Time (sec)	Ave. Temp. (^{o}C)	No. of Tests	Sulfur Release (fraction) Measured	Predicted	Residual SS ($\times 10^{-3}$)	LOF SS ($\times 10^{-3}$)
4.5	274	10	0.047	0.033	11.29	1.96
4.5	327	10	0.110	0.078	49.85	10.24
4.5	448	10	0.292	0.259	74.74	10.89
4.5	513	7	0.282	0.267	3.62	1.58
4.5	566	17	0.219	0.233	53.42	3.33
9.0	437	14	0.311	0.336	16.33	8.75
9.0	517	11	0.358	0.326	29.24	10.24
9.0	572	11	0.285	0.253	30.25	11.26
10.5	277	10	0.078	0.075	18.13	0.09
10.5	326	10	0.139	0.148	35.08	0.81
10.5	451	10	0.360	0.373	34.73	1.69
10.5	555	10	0.240	0.278	37.40	14.44
10.5	734	10	0.132	0.131	23.41	0.01
15.0	276	10	0.089	0.099	22.11	1.00
15.0	328	10	0.193	0.198	21.70	0.25
15.0	453	10	0.434	0.406	33.28	7.84
15.0	563	10	0.248	0.268	31.45	4.00
15.0	732	10	0.131	0.131	8.47	0.00

Table 28. Lack-of-fit analysis, sulfide model.

Time (sec)	Ave. Temp. (°C)	No. of Tests	Sulfur Release (fraction) Measured	Predicted	Residual SS ($\times 10^{-3}$)	LOF SS ($\times 10^{-3}$)
4.5	319	7	0.051	0.028	21.12	3.70
4.5	369	5	0.127	0.088	14.48	7.61
4.5	426	8	0.341	0.300	29.11	13.44
4.5	474	9	0.350	0.393	87.32	16.64
4.5	536	6	0.233	0.250	14.67	1.73
4.5	684	7	0.093	0.082	8.43	0.85
9.0	324	6	0.124	0.056	45.60	27.74
9.0	373	7	0.128	0.194	70.78	30.49
9.0	441	8	0.370	0.390	199.70	3.20
9.0	471	16	0.431	0.400	147.77	15.38
9.0	518	5	0.261	0.307	43.50	10.58
9.0	679	7	0.073	0.084	7.40	0.85
15.0	324	6	0.095	0.088	11.03	0.15
15.0	374	5	0.257	0.264	77.44	0.24
15.0	426	9	0.415	0.391	167.30	5.18
15.0	480	9	0.375	0.402	82.99	5.62
15.0	542	6	0.259	0.236	34.58	3.17
15.0	678	7	0.088	0.085	3.96	0.06

Table 29. Pyrolysis of soda liquors containing thiosulfate and sulfide. (Pyrolysis Time = 9.0 Seconds)

Liquor #	Temperature (°C)	Sulfur Released (mg S/100 g solids)
1	454	741
	406	749
	441	689
	422	880
	442	887
	472	860
	421	776
	430	854
2	460	883
	402	571
	427	943
	484	659
	430	1043
	412	887
	433	990
	414	690
	419	807
	429	590

Table 30. Pyrolysis of kraft black liquors
(Pyrolysis Time = 9.0 Seconds)

Liquor #	Temperature (°C)	Sulfur Released (mg S/100 g solids)
1	434	796
	456	1043
	435	987
	459	1219
	440	1120
	452	1248
	433	1223
	456	1221
	435	970
	466	1095
2	460	733
	463	754
	453	810
	457	1216
	468	1169
	467	1276
	467	1052
3	495	1121
	466	1627
	467	1197
	453	1511
	480	1814
	472	1568
	499	1295
4	418	1340
	416	1594
	463	1325
	435	1333
	441	1660
	407	1358
	421	1412

APPENDIX 3. EXPERIMENTAL RESULTS USED IN HEAT TRANSFER MODEL.

Listed below are the results of the individual tests used to determine the swelling properties of the black liquors used in the heat transfer experiments and the results of experiments used to determine the effect of particle size, solids content, and degree of swelling on sulfur release.

Table 31. Swelling properties of liquors used in heat transfer study.

Liq #	Solids (%)	Drop Wt (mg)	Swollen Vol. (cc)	Swelling (cc/g sol)
1	62.7	14.2	1.102	77.6
		10.5	.808	77.0
		12.9	.749	58.0
		8.8	.420	47.8
		8.2	.315	38.4
		11.0	.586	53.2
		14.9	.697	46.8
		8.4	.378	45.0
2	66.9	10.2	.528	51.8
		6.7	.382	57.1
		11.3	.672	59.5
		8.2	.488	59.5
		9.8	.372	38.0
		7.0	.329	47.1
		8.6	.426	49.5
		11.0	.560	50.9
3	74.0	12.8	.619	48.3
		9.0	.349	38.8
		10.2	.523	51.3
		10.8	.441	40.8
		7.5	.386	51.5
		11.5	.555	48.2
		9.3	.594	63.9
		13.5	.499	37.0
		13.2	.455	34.5
4	74.0	13.0	.301	23.2
		11.4	.293	25.7
		10.5	.267	25.4
		14.2	.388	27.3
		8.4	.133	15.8
		12.4	.256	20.6
		13.8	.337	24.4
		11.6	.276	23.8
		8.8	.244	27.8

Table 32. Sulfur release during kraft black liquor pyrolysis. Drop Weight in mg solids, Sulfur Release in mg S/100 g solids Gas Temperature = 665° C

63.4% Solids Liquor

Drop Weight	Sulfur Release	Drop Weight	Sulfur Release	Drop Weight	Sulfur Release
6.5	496	13.0	507	24.2	624
6.6	527	12.5	544	24.2	766
6.1	725	13.2	651	25.9	664
6.6	495	12.5	651	24.7	707
6.5	503	12.2	654	24.3	1053
6.6	505	11.9	356	25.7	945
6.0	569	13.0	426	23.8	910

77.8% Solids Liquor

Drop Weight	Sulfur Release	Drop Weight	Sulfur Release	Drop Weight	Sulfur Release
8.4	448	14.4	792	30.4	897
7.4	497	14.1	498	30.5	866
7.8	653	15.6	789	31.1	863
7.8	565	14.1	785	30.7	861
7.7	713	15.3	750	30.3	681
7.8	608	16.1	843	31.0	1048
8.1	774	14.9	820	30.7	1020

76.7% Solids Liquor; Swelling Retardant Added

Drop Weight	Sulfur Release	Drop Weight	Sulfur Release	Drop Weight	Sulfur Release
7.3	385	15.5	452	29.6	712
8.4	728	15.8	785	29.1	1012
7.0	713	15.6	820	29.9	773
8.0	508	14.1	781	29.2	935
8.3	932	14.2	756	29.5	799
8.0	635	15.2	764	29.1	990
8.1	602	14.1	760	29.5	896

APPENDIX 4. PROGRAMS USED TO CALCULATE KINETIC PARAMETERS.

Below are the computer programs used to calculate the kinetic parameters for the thiosulfate and sulfide models. The data files used by the various programs are also included.

KT1

```
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FILE  1(KIND=DISK,TITLE="KDT1",FILETYPE=8)                               00000200
FILE  8(KIND=PRINTER)                                                    00000300
$INCLUDE "*IMSL/ZXMWD"                                                   00000400
$INCLUDE "*IMSL/UERSET"                                                  00000500
$INCLUDE "*IMSL/UERTST"                                                  00000600
$INCLUDE "*IMSL/UGETIO"                                                  00000700
$INCLUDE "*IMSL/ZSRCH"                                                   00000800
$INCLUDE "*IMSL/ZXMIN"                                                   00000900
$INCLUDE "*IMSL/ZXMWE"                                                   00001000
$INCLUDE "*IMSL/USPKD"                                                   00001100
C                                                                        00001200
C     THIS PROGRAM IS DESIGNED TO CALCULATE THE OPTIMUM VALUES OF        00001300
C     VMAX K0 AND E0 FROM VALUES OF TEMP AND TIME ENTERED.               00001400
C                                                                        00001500
      EXTERNAL FCN                                                       00001600
      REAL WORK(39),A(3),B(3),X(3),F                                     00001700
      INTEGER N,NSIG,NSRCH,IWORK(3),IER                                  00001800
      COMMON TE(104),TI(104),VACT(104),VCAL(104),FM                      00001900
C                                                                        00002000
C     READ THE DATA FILE                                                 00002100
C                                                                        00002200
      READ(1,/)(A(I),I=1,3),(B(J),J=1,3),(TE(K),K=1,104),                00002300
     !(TI(L),L=1,104),(VACT(M),M=1,104)                                  00002400
      DO 33 I=1,104                                                      00002410
      TE(I)=TE(I)+273.                                                   00002420
   33 CONTINUE                                                           00002430
C                                                                        00002500
C     SET THE PARAMETERS FOR THE IMSL ROUTINE ZXMWD                      00002600
C                                                                        00002700
      FM=1.0E50                                                          00002800
      N=3                                                                00002900
      NSIG=3                                                             00003000
      NSRCH=25                                                           00003100
      CALL ZXMWD(FCN,N,NSIG,A,B,NSRCH,X,F,WORK,IWORK,IER)                00003200
C                                                                        00003300
C     CHECK FOR ERRORS                                                   00003400
C                                                                        00003500
      IF(IER.NE.0)GOTO 10                                                00003600
C                                                                        00003700
C     PRINT OUT RESULTS                                                  00003800
C                                                                        00003900
      WRITE(8,101)X(1),X(2),X(3),F                                       00004000
  101 FORMAT(1X,"K0   = ",E20.4,/,1X,"E0   = ",                          00004100
     !E20.4,/,1X,"VMAX = ",E20.4,/1X,"ER   = ",E20.4)                    00004200
      WRITE(8,104)                                                       00004300
  104 FORMAT(1X,//,1X," VCAL",7X,"VACT",/)                               00004400
      DO 50 I=1,104                                                      00004500
      WRITE(8,105)VCAL(I),VACT(I)                                        00004600
  105 FORMAT(1X,F6.4,5X,F6.4)                                            00004700
```

```
   50 CONTINUE                                                          00004800
      GOTO 20                                                           00004900
C                                                                       00005000
C     ERROR ENCOUNTERED                                                 00005100
C                                                                       00005200
   10 WRITE(6,102)IER                                                   00005300
  102 FORMAT(1X,"ERROR = ",I3)                                          00005400
   20 STOP                                                              00005500
      END                                                               00005600
C                                                                       00005700
C     SUBROUTINE FCN TO CALCULATE THE VALUES OF F                       00005800
C                                                                       00005900
      SUBROUTINE FCN(N,X,F)                                             00006000
      REAL X(3),F,T(4)                                                  00006100
      INTEGER N                                                         00006200
      COMMON TE(104),TI(104),VACT(104),VCAL(104),FM                     00006300
      F=0.0                                                             00006400
      R=1.987E-03                                                       00006410
      DO 30 I=1,104                                                     00006500
      DT=(TE(I)-523.)/5.                                                00006505
      DO 60 J=1,4                                                       00006510
      T(J)=523.+DT*J                                                    00006520
   60 CONTINUE                                                          00006530
      VCAL(I)=X(3)-X(3)*(EXP(-X(1)*(TI(I)*EXP(-X(2)/R/TE(I))+           00006600
     !(DT/3973.+DT/84.)*(.5*EXP(-X(2)/R/523.)+EXP(-X(2)/R/T(1))+        00006700
     !EXP(-X(2)/R/T(2))+EXP(-X(2)/R/T(3))+EXP(-X(2)/R/T(4))+            00006800
     !.5*EXP(-X(2)/R/TE(I))))))                                         00006900
C                                                                       00007200
C     CALCULATE VOLATILES RELEASED; COMPARE TO ACTUAL DATA              00007300
C     SUM THE SQUARE OF THE ERRORS                                      00007400
C                                                                       00007500
      F=F+(VACT(I)-VCAL(I))**2                                          00007600
   30 CONTINUE                                                          00007700
C                                                                       00007800
C     IF ERROR IS SMALLEST YET ENCOUNTERED, PRINT OUT CONSTANTS         00007900
C                                                                       00008000
      FM=AMIN1(F,FM)                                                    00008100
      IF(FM.NE.F)GOTO 40                                                00008200
      WRITE(6,/)X(1),X(2),X(3),F                                        00008300
   40 RETURN                                                            00008400
      END                                                               00008500
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$INCLUDE "*IMSL/UERSET"                                                  00000500
$INCLUDE "*IMSL/UERTST"                                                  00000600
$INCLUDE "*IMSL/UGETIO"                                                  00000700
$INCLUDE "*IMSL/ZSRCH"                                                   00000800
$INCLUDE "*IMSL/ZXMJN"                                                   00000900
$INCLUDE "*IMSL/ZXMWE"                                                   00001000
$INCLUDE "*IMSL/USPKD"                                                   00001100
C                                                                        00001200
C     THIS PROGRAM IS DESIGNED TO CALCULATE THE OPTIMUM VALUES OF        00001300
C     A AND B FROM VALUES OF RELEASE TEMP AND TIME ENTERED.              00001400
C                                                                        00001500
      EXTERNAL FCN                                                       00001600
      REAL WORK(25),A(2),B(2),X(2),F                                     00001700
      INTEGER N,NSIG,NSRCH,IWORK(2),IER                                  00001800
      COMMON TE(86),TI(86),VACT(86),VCAL(86),VH(86),FM                   00001900
C                                                                        00002000
C     READ THE DATA FILE                                                 00002100
C                                                                        00002200
      READ(1,/)(A(I),I=1,2),(B(J),J=1,2),(TE(K),K=1,86),                 00002300
     !(TI(L),L=1,86),(VACT(M),M=1,86)                                    00002400
      DO 33 I=1,86                                                       00002410
      TE(I)=TE(I)+273.                                                   00002420
   33 CONTINUE                                                           00002430
C                                                                        00002500
C     SET THE PARAMETERS FOR THE IMSL ROUTINE ZXMWD                      00002600
C                                                                        00002700
      FM=1.0E50                                                          00002800
      N=2                                                                00002900
      NSIG=3                                                             00003000
      NSRCH=25                                                           00003100
      CALL ZXMWD(FCN,N,NSIG,A,B,NSRCH,X,F,WORK,IWORK,IER)                00003200
C                                                                        00003300
C     CHECK FOR ERRORS                                                   00003400
C                                                                        00003500
      IF(IER.NE.0)GOTO 10                                                00003600
C                                                                        00003700
C     PRINT OUT RESULTS                                                  00003800
C                                                                        00003900
      WRITE(8,101)X(1),X(2),F                                            00004000
  101 FORMAT(1X,"A = ",E20.4,/,1X,"B   = ",E20.4,                        00004100
     !/,1X,"ER   = ",E20.4)                                              00004200
      WRITE(8,104)                                                       00004300
  104 FORMAT(1X,//,1X," VCAL",7X,"VACT",/)                               00004400
      DO 50 I=1,86                                                       00004500
      WRITE(8,105)VCAL(I),VACT(I)                                        00004600
  105 FORMAT(1X,F6.4,5X,F6.4)                                            00004700
```

```
   50 CONTINUE                                                          00004800
      GOTO 20                                                           00004900
C                                                                       00005000
C     ERROR ENCOUNTERED                                                 00005100
C                                                                       00005200
   10 WRITE(6,102)IER                                                   00005300
  102 FORMAT(1X,"ERROR = ",I3)                                          00005400
   20 STOP                                                              00005500
      END                                                               00005600
C                                                                       00005700
C     SUBROUTINE FCN TO CALCULATE THE VALUES OF F                       00005800
C                                                                       00005900
      SUBROUTINE FCN(N,X,F)                                             00006000
      REAL X(2),F,T(4)                                                  00006100
      INTEGER N,IERR                                                    00006200
      COMMON TE(86),TI(86),VACT(86),VCAL(86),VH(86),FM                  00006300
C                                                                       00006400
C     SOLVE FOR THE AMOUNT OF SULFUR RLEASED DURING THE CONSTANT        00006500
C     TEMPERATURE AND HEATUP PORTIONS                                   00006600
C                                                                       00006700
      F=0.0                                                             00006800
      R=1.987E-03                                                       00006900
      VMAX=.4339                                                        00007000
      AK0=255.08                                                        00007100
      E=10.49                                                           00007200
      DO 30 I=1,86                                                      00007300
      DI=(TE(I)-523.)/5.                                                00007400
      DO 60 J=1,4                                                       00007500
      T(J)=523.+DI*J                                                    00007600
   60 CONTINUE                                                          00007700
      AKEQ=EXP(X(1)/TE(I)-X(2))                                         00007710
      IF(AKEQ.GT.1.0)AKEQ=1.0                                           00007720
      VH(I)=VMAX*AKEQ-VMAX*AKEQ*(EXP(-AK0*DI/3973.*                     00007800
     !(.5*EXP(-E/R/523.)+EXP(-E/R/T(1))+EXP(-E/R/T(2))+                 00007900
     !EXP(-E/R/T(3))+EXP(-E/R/T(4))+.5*EXP(-E/R/TE(I)))))               00008000
      C1=EXP(-AK0*TI(I)*EXP(-E/R/TE(I)))                                00008100
      VCAL(I)=VMAX*AKEQ*(1.-C1)                                         00008200
      VCAL(I)=VCAL(I)+VH(I)                                             00008210
C                                                                       00008300
C     CALCULATE VOLATILES RELEASED; COMPARE TO ACTUAL DATA              00008400
C     SUM THE SQUARE OF THE ERRORS                                      00008500
C                                                                       00008600
      F=F+(VACT(I)-VCAL(I))**2                                          00008700
   30 CONTINUE                                                          00008800
C                                                                       00008900
C     IF ERROR IS SMALLEST YET ENCOUNTERED, PRINT OUT CONSTANTS         00009000
C                                                                       00009100
      FM=AMIN1(F,FM)                                                    00009200
      IF(FM.NE.F)GOTO 40                                                00009300
      WRITE(6,/)X(1),X(2),F                                             00009400
   40 RETURN                                                            00009500
      END                                                               00009600
```

KDT2

1000.
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KS1

```
$RESET FREE                                                              00000100
FILE  1(KIND=DISK,TITLE="KDS1",FILETYPE=8)                               00000200
FILE  8(KIND=PRINTER)                                                    00000300
$INCLUDE "*IMSL/ZXMWD"                                                   00000400
$INCLUDE "*IMSL/UERSET"                                                  00000500
$INCLUDE "*IMSL/UERTST"                                                  00000600
$INCLUDE "*IMSL/UGETIO"                                                  00000700
$INCLUDE "*IMSL/ZSRCH"                                                   00000800
$INCLUDE "*IMSL/ZXMDN"                                                   00000900
$INCLUDE "*IMSL/ZXMWE"                                                   00001000
$INCLUDE "*IMSL/USPKD"                                                   00001100
C                                                                        00001200
C     THIS PROGRAM IS DESIGNED TO CALCULATE THE OPTIMUM VALUES OF        00001300
C     K0 AND E0 FROM VALUES OF TEMP AND TIME ENTERED.                    00001400
C                                                                        00001500
      EXTERNAL FCN                                                       00001600
      REAL WORK(39),A(3),B(3),X(3),F                                     00001700
      INTEGER N,NSIG,NSRCH,IWORK(3),IER                                  00001800
      COMMON TE(92),TI(92),VACT(92),VCAL(92),FM                          00001900
C                                                                        00002000
C     READ THE DATA FILE                                                 00002100
C                                                                        00002200
      READ(1,/)(A(I),I=1,3),(B(J),J=1,3),(TE(K),K=1,92),                 00002300
     !(TI(L),L=1,92),(VACT(M),M=1,92)                                    00002400
      DO 33 I=1,92                                                       00002500
      TE(I)=TE(I)+273.                                                   00002600
   33 CONTINUE                                                           00002700
C                                                                        00002800
C     SET THE PARAMETERS FOR THE IMSL ROUTINE ZXMWD                      00002900
C                                                                        00003000
      FM=1.0E50                                                          00003100
      N=3                                                                00003200
      NSIG=3                                                             00003300
      NSRCH=25                                                           00003400
      CALL ZXMWD(FCN,N,NSIG,A,B,NSRCH,X,F,WORK,IWORK,IER)                00003500
C                                                                        00003600
C     CHECK FOR ERRORS                                                   00003700
C                                                                        00003800
      IF(IER.NE.0)GOTO 10                                                00003900
C                                                                        00004000
C     PRINT OUT RESULTS                                                  00004100
C                                                                        00004200
      WRITE(8,101)X(1),X(2),X(3),F                                       00004300
  101 FORMAT(1X,"K0   = ",E20.4,/,1X,"E0   = ",                          00004400
     !E20.4,/,1X,"VMAX = ",E20.4,/1X,"ER   = ",E20.4)                    00004500
      WRITE(8,104)                                                       00004600
  104 FORMAT(1X,//,1X," VCAL",7X,"VACT",/)                               00004700
      DO 50 I=1,92                                                       00004800
      WRITE(8,105)VCAL(I),VACT(I)                                        00004900
  105 FORMAT(1X,F6.4,5X,F6.4)                                            00005000
```

```
   50 CONTINUE                                                          00005100
      GOTO 20                                                           00005200
C                                                                       00005300
C     ERROR ENCOUNTERED                                                 00005400
C                                                                       00005500
   10 WRITE(6,102)IER                                                   00005600
  102 FORMAT(1X,"ERROR = ",I3)                                          00005700
   20 STOP                                                              00005800
      END                                                               00005900
C                                                                       00006000
C     SUBROUTINE FCN TO CALCULATE THE VALUES OF F                       00006100
C                                                                       00006200
      SUBROUTINE FCN(N,X,F)                                             00006300
      REAL X(3),F,T(4)                                                  00006400
      INTEGER N                                                         00006500
      COMMON TE(92),TI(92),VACT(92),VCAL(92),FM                         00006600
      F=0.0                                                             00006700
      R=1.987E-03                                                       00006800
      DO 30 I=1,92                                                      00006900
      DT=(TE(I)-523.)/5.                                                00007000
      DO 60 J=1,4                                                       00007100
      T(J)=523.+DT*J                                                    00007200
   60 CONTINUE                                                          00007300
      VCAL(I)=X(3)-X(3)*(EXP(-X(1)*(TI(I)*EXP(-X(2)/R/TE(I))+           00007400
     !(DT/3973.+DT/84.)*(.5*EXP(-X(2)/R/523.)+EXP(-X(2)/R/T(1))+        00007500
     !EXP(-X(2)/R/T(2))+EXP(-X(2)/R/T(3))+EXP(-X(2)/R/T(4))+            00007600
     !.5*EXP(-X(2)/R/TE(I))))))                                         00007700
C                                                                       00007800
C     CALCULATE VOLATILES RELEASED; COMPARE TO ACTUAL DATA              00007900
C     SUM THE SQUARE OF THE ERRORS                                      00008000
C                                                                       00008100
      F=F+(VACT(I)-VCAL(I))**2                                          00008200
   30 CONTINUE                                                          00008300
C                                                                       00008400
C     IF ERROR IS SMALLEST YET ENCOUNTERED, PRINT OUT CONSTANTS         00008500
C                                                                       00008600
      FM=AMIN1(F,FM)                                                    00008700
      IF(FM.NE.F)GOTO 40                                                00008800
      WRITE(6,/)X(1),X(2),X(3),F                                        00008900
   40 RETURN                                                            00009000
      END                                                               00009100
```

KDS1

1.0E05
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KS2

```
$RESET FREE                                                              00000100
FILE  1(KIND=DISK,TITLE="KDS2",FILETYPE=8)                               00000200
FILE  8(KIND=PRINTER)                                                    00000300
$INCLUDE "*IMSL/ZXMWD"                                                   00000400
$INCLUDE "*IMSL/UERSET"                                                  00000500
$INCLUDE "*IMSL/UERIST"                                                  00000600
$INCLUDE "*IMSL/UGETIO"                                                  00000700
$INCLUDE "*IMSL/ZSRCH"                                                   00000800
$INCLUDE "*IMSL/ZXMIN"                                                   00000900
$INCLUDE "*IMSL/ZXMWE"                                                   00001000
$INCLUDE "*IMSL/USPKD"                                                   00001100
C                                                                        00001200
C     THIS PROGRAM IS DESIGNED TO CALCULATE THE OPTIMUM VALUES OF        00001300
C     A AND B FROM VALUES OF RELEASE TEMP AND TIME ENTERED.              00001400
C                                                                        00001500
      EXTERNAL FCN                                                       00001600
      REAL WORK(25),A(2),B(2),X(2),F                                     00001700
      INTEGER N,NSIG,NSRCH,IWORK(2),IER                                  00001800
      COMMON TE(41),TI(41),VACT(41),VCAL(41),VH(41),FM                   00001900
C                                                                        00002000
C     READ THE DATA FILE                                                 00002100
C                                                                        00002200
      READ(1,/)(A(I),I=1,2),(B(J),J=1,2),(TE(K),K=1,41),                 00002300
     !(TI(L),L=1,41),(VACT(M),M=1,41)                                    00002400
      DO 33 I=1,41                                                       00002410
      TE(I)=TE(I)+273.                                                   00002420
   33 CONTINUE                                                           00002430
C                                                                        00002500
C     SET THE PARAMETERS FOR THE IMSL ROUTINE ZXMWD                      00002600
C                                                                        00002700
      FM=1.0E50                                                          00002800
      N=2                                                                00002900
      NSIG=3                                                             00003000
      NSRCH=25                                                           00003100
      CALL ZXMWD(FCN,N,NSIG,A,B,NSRCH,X,F,WORK,IWORK,IER)                00003200
C                                                                        00003300
C     CHECK FOR ERRORS                                                   00003400
C                                                                        00003500
      IF(IER.NE.0)GOTO 10                                                00003600
C                                                                        00003700
C     PRINT OUT RESULTS                                                  00003800
C                                                                        00003900
      WRITE(8,101)X(1),X(2),F                                            00004000
  101 FORMAT(1X,"A = ",E20.4,/,1X,"B = ",E20.4,                          00004100
     !/,1X,"ER= ",E20.4)                                                 00004200
      WRITE(8,104)                                                       00004300
  104 FORMAT(1X,//,1X," VCAL",7X,"VACT",/)                               00004400
      DO 50 I=1,41                                                       00004500
      WRITE(8,105)VCAL(I),VACT(I)                                        00004600
  105 FORMAT(1X,F6.4,5X,F6.4)                                            00004700
```

```
   50 CONTINUE                                                          00004800
      GOTO 20                                                           00004900
C                                                                       00005000
C     ERROR ENCOUNTERED                                                 00005100
C                                                                       00005200
   10 WRITE(6,102)IER                                                   00005300
  102 FORMAT(1X,"ERROR = ",I3)                                          00005400
   20 STOP                                                              00005500
      END                                                               00005600
C                                                                       00005700
C     SUBROUTINE FCN TO CALCULATE THE VALUES OF F                       00005800
C                                                                       00005900
      SUBROUTINE FCN(N,X,F)                                             00006000
      REAL X(2),F,T(4)                                                  00006100
      INTEGER N,IERR                                                    00006200
      COMMON TE(41),TI(41),VACT(41),VCAL(41),VH(41),FM                  00006300
C                                                                       00006400
C     SOLVE FOR THE AMOUNT OF SULFUR RELEASED DURING THE CONSTANT       00006500
C     TEMPERATURE AND HEATUP PORTIONS                                   00006600
C                                                                       00006700
      F=0.0                                                             00006800
      R=1.987E-03                                                       00006900
      VMAX=.4020                                                        00007000
      AK0=9692470.                                                      00007100
      E=24.099                                                          00007200
      DO 30 I=1,41                                                      00007300
      DT=(TE(I)-523.)/5.                                                00007400
      DO 60 J=1,4                                                       00007500
      T(J)=523.+DT*J                                                    00007600
   60 CONTINUE                                                          00007700
      AKEQ=EXP(X(1)/TE(I)-X(2))                                         00007710
      IF(AKEQ.GT.1.0)AKEQ=1.0                                           00007720
      VH(I)=VMAX*AKEQ-VMAX*AKEQ*(EXP(-AK0*DT/3973.*                     00007800
     !(.5*EXP(-E/R/523.)+EXP(-E/R/T(1))+EXP(-E/R/T(2))+                 00007900
     !EXP(-E/R/T(3))+EXP(-E/R/T(4))+.5*EXP(-E/R/TE(I)))))               00008000
      C1=EXP(-AK0*TI(I)*EXP(-E/R/TE(I)))                                00008100
      VCAL(I)=VMAX*AKEQ*(1.-C1)                                         00008200
      VCAL(I)=VCAL(I)+VH(I)                                             00008210
C                                                                       00008300
C     CALCULATE VOLATILES RELEASED; COMPARE TO ACTUAL DATA              00008400
C     SUM THE SQUARE OF THE ERRORS                                      00008500
C                                                                       00008600
      F=F+(VACT(I)-VCAL(I))**2                                          00008700
   30 CONTINUE                                                          00008800
C                                                                       00008900
C     IF ERROR IS SMALLEST YET ENCOUNTERED, PRINT OUT CONSTANTS         00009000
C                                                                       00009100
      FM=AMIN1(F,FM)                                                    00009200
      IF(FM.NE.F)GOTO 40                                                00009300
      WRITE(6,/)X(1),X(2),F                                             00009400
   40 RETURN                                                            00009500
      END                                                               00009600
```

KDS2

6000.
8.00
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10.00
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.049
.044
.076
.047
.244
.181
.298
.348
.169
.339
.055
.080
.062
.107
.127
.101
.086

APPENDIX 5. HEAT TRANSFER MODELING PROGRAM.

The program BLHCAL is listed below. This program calculates the temperature of a three-layer black liquor drop during pyrolysis in an inert atmosphere. The inputs to the program are found in the data file BLDTA and include:

Drop's Dry Weight (grams)

Drop's Solids Content (fraction)

Drop's Swelling Parameter (cc/g solids)

Nominal Gas Flow (cc/sec)

Gas Temperature (^{o}C)

Wall Temperature (^{o}C)

BLTCAL

```
$RESET FREE                                                              00000100
FILE  1(KIND=DISK,TITLE="BLDTA",FILETYPE=8)                              00000200
FILE  5(KIND=REMOTE,MYUSE=IN)                                            00000300
FILE  6(KIND=REMOTE,MYUSE=OUT )                                          00000400
FILE  8(KIND=PRINTER)                                                    00000500
$INCLUDE "*IMSL/DVERK"                                                   00000600
$INCLUDE "*IMSL/UERTST"                                                  00000700
$INCLUDE "*IMSL/UGETIO"                                                  00000800
$INCLUDE "*IMSL/USPKD"                                                   00000900
C                                                                        00001000
C     PROGRAM TO DETERMINE THE TEMPERATURE OF A 3-LAYER BLACK LIQUOR     00001100
C     DROPLET DURING PYROLYSIS.  THE PROGRAM ASSUMES LINEAR SWELLING     00001200
C     BETWEEN 250-500 C.                                                 00001300
C                                                                        00001400
      EXTERNAL FCN                                                       00001500
      DIMENSION Y(3),C(24),W(3,9),Y0(3)                                  00001600
      COMMON FM(3),DIA(3),AML0(3),R(3),ANU,AKG,TG,EM,F,                  00001700
     !TR,HP,S0,SR,SW,RHO,V0(3),ROD(3),VOD(3),RHOD                        00001800
C                                                                        00001900
C     READ THE DATA FILE                                                 00002000
C                                                                        00002100
      READ(1,/) AM0,S0,SW,VG0,TG,TR                                      00002200
C                                                                        00002300
C     CALCULATE DROPLET DIMENSIONS-USE EQUAL MASS LAYERS                 00002400
C                                                                        00002500
      RHO=1.0+.4137*S0+4.0715E-2*S0**2                                   00002600
      WM0=AM0/S0-AM0                                                     00002700
      R(1)=((AM0+WM0)*3./(4.*RHO*3.14159))**.33333                       00002800
      R(2)=(2./3.*(AM0+WM0)*3./(4.*RHO*3.14159))**.33333                 00002900
      R(3)=(1./3.*(AM0+WM0)*3./(4.*RHO*3.14159))**.33333                 00003000
      DO 15 I=1,3                                                        00003100
      AML0(I)=AM0/3.                                                     00003200
      V0(I)=4./3.*3.14159*R(I)**3                                        00003300
      ROD(I)=R(I)*1.5                                                    00003400
      VOD(I)=4./3.*3.14159*ROD(I)**3                                     00003500
   15 CONTINUE                                                           00003600
      RHOD=AML0(3)/VOD(3)                                                00003700
      SR=.82-.0003*TG                                                    00003800
      TGK=TG+273.                                                        00003900
C                                                                        00004000
C     CALCULATE GAS FLOW PARAMETERS                                      00004100
C                                                                        00004200
      VG=TGK*VG0/298.                                                    00004300
      AMG=VG/(TGK*82.06)*28.                                             00004400
      VEL=VG/26.01                                                       00004500
      RHOG=AMG/VG                                                        00004600
      VISC=3.255E-07*TG+1.887E-04                                        00004700
      RE=R(1)*2*VEL*RHOG/VISC                                            00004800
      CPG=4.417E-05*TG+.2504                                             00004900
      AKG=1.051E-07*TG+7.118E-05                                         00005000
```

```
      PR=CPG*VISC/AKG                                                   00005100
      ANU=2.+.6*RE**.5*PR**.3333                                        00005200
C                                                                       00005300
C     CALCULATE THE DRYING LOAD, HEAT SUPPLIED, AND TIME TO DRY         00005400
C                                                                       00005500
      DOD=ROD(1)*2.                                                     00005600
      QDRY=35.00*AM0+554.73*WM0                                         00005700
      QC=3.14159*DOD**2*ANU*AKG/DOD*(TG-150.)                           00005800
      QR=3.14159*DOD**2*.9*1.35E-12*((TR+273.)**4-3.20156E10)           00005900
      TTD=QDRY/(QC+QR)*10.                                              00006000
C                                                                       00006100
C     SET THE INITIAL CONDITIONS.  CALL THE ROUTINE DVERK TO CALCULATE  00006200
C     THE TEMPERATURES.  PRINT THE RESULTS.                             00006300
C                                                                       00006400
      NW=3                                                              00006500
      N=3                                                               00006600
      X=0.0                                                             00006700
      Y(1)=150.                                                         00006800
      Y(2)=150.                                                         00006900
      Y(3)=150.                                                         00007000
      TOL=.01                                                           00007100
      IND=1                                                             00007200
      XE=0.0                                                            00007300
      DO 25 I=1,3                                                       00007400
      DIA(I)=R(I)*20.                                                   00007500
      FM(I)=AML0(I)*1000.                                               00007600
      Y0(I)=100.0                                                       00007700
   25 CONTINUE                                                          00007800
      WRITE(8,101)                                                      00007900
  101 FORMAT(1X,"   TIME   TS     TM     TI     MS     MM     ",       00008000
     !"MI     DS     DM     DI",/,1X,"   (SEC)  (C)    (C)    (C)    ", 00008100
     !"(MG)   (MG)   (MG)   (MM)   (MM)   (MM)")                       00008200
      WRITE(8,102)XE,Y0(1),Y0(2),Y0(3),FM(1),FM(2),FM(3),               00008300
     !DIA(1),DIA(2),DIA(3)                                              00008400
  102 FORMAT(1X,10F7.2)                                                 00008500
      DO 80 NO=1,400                                                    00008600
      TNO=NO*1.                                                         00008700
      DIA(1)=ROD(1)*20.                                                 00008800
      DIA(2)=ROD(2)*20.                                                 00008900
      DIA(3)=ROD(3)*20.                                                 00009000
      IF(TNO.LE.TTD)GO TO 50                                            00009100
      XEND=(TNO-TTD)/10.                                                00009200
      CALL DVERK(N,FCN,X,Y,XEND,TOL,IND,C,NW,W,IER)                     00009300
      IF(IND.LT.0.OR.IER.GT.0)GO TO 10                                  00009400
   50 IF(AMOD(TNO,10.).NE.0.0)GO TO 80                                  00009500
      TINO=TNO/10.                                                      00009600
      WRITE(8,102)TINO,Y(1),Y(2),Y(3),FM(1),FM(2),FM(3),                00009700
     !DIA(1),DIA(2),DIA(3)                                              00009800
   80 CONTINUE                                                          00009900
      GO TO 20                                                          00010000
C                                                                       00010100
C     CHECK FOR ERRORS                                                  00010200
```

```
C                                                                       00010300
   10 WRITE(6,103)                                                      00010400
  103 FORMAT(1X," ERROR DETECTED!")                                     00010500
      WRITE(6,104)IND,IER                                               00010600
  104 FORMAT(1X,"IND= ",I3," IER= ",I3)                                 00010700
   20 STOP                                                              00010800
      END                                                               00010900
C                                                                       00011000
C     SUBROUTINE FUNCTION TO CALCULATE THE DIFFERENTIAL EQUATION        00011100
C                                                                       00011200
      SUBROUTINE FCN(N,X,Y,YPRIME)                                      00011300
      COMMON FM(3),DIA(3),AMLO(3),R(3),ANU,AKG,TG,EM,F,                 00011400
     !TR,HP,SO,SR,SW,RHO,VO(3),ROD(3),VOD(3),RHOD                       00011500
      REAL X,Y(3),YPRIME(3),DN(3),RN(3),AK(3),RHG(3),VIN(3),            00011600
     !CPS(3),AKS(3),B(3),AM(3),RHC(3),P(3),AKC(3),PSC(3)                00011700
      INTEGER N                                                         00011800
C                                                                       00011900
C     CALCULATE TEMPERATURE-DEPENDENT BLACK LIQUOR PARAMETERS AND       00012000
C     THE HEAT TRANSFER TERMS                                           00012100
C                                                                       00012200
      F=1.0                                                             00012300
      EM=.75                                                            00012400
      DO 35 I=1,3                                                       00012500
      HP=-150.0                                                         00012600
      CPS(I)=0.7                                                        00012700
      AKS(I)=5.E-06*Y(I)-2.E-4                                          00012800
      B(I)=(1.1365+.2065/(R(1)*2.)-4.0625*SO+5.062E-03*Y(I))*           00012900
     !AMLO(I)/100.                                                      00013000
      IF(B(I).LT.0.0)B(I)=0.0                                           00013100
      IF(Y(I).LT.250.)B(I)=0.0                                          00013200
      AM(I)=AMLO(I)-B(I)*X                                              00013300
      PSR=AM(I)/AMLO(I)                                                 00013400
      IF(PSR.GT.SR)GO TO 45                                             00013500
      AM(I)=AMLO(I)*SR                                                  00013600
      B(I)=0.0                                                          00013700
   45 FM(I)=AM(I)*1000.                                                 00013800
   35 CONTINUE                                                          00013900
C                                                                       00014000
C     CALCULATE THE NEW RADII AND DIAMETERS                             00014100
C                                                                       00014200
      DVOL= SW*AMLO(3)-VOD(3)                                           00014300
      DO 60 I=1,3                                                       00014400
      PSC(I)=(Y(I)-250.)/250.                                           00014500
      IF(PSC(I).GT.1.)PSC(I)=1.                                         00014600
      IF(PSC(I).LT.0.)PSC(I)=0.                                         00014700
      VIN(I)=PSC(I)*DVOL+VOD(3)                                         00014800
   60 CONTINUE                                                          00014900
      RN(3)=(VIN(3)*3./(4.*3.14159))**.33333                            00015000
      RN(2)=((VIN(3)+VIN(2))*3./(4.*3.14159))**.33333                   00015100
      RN(1)=((VIN(3)+VIN(2)+VIN(1))*3./(4.*3.14159))**.33333            00015200
      DO 65 I=1,3                                                       00015300
      DN(I)=RN(I)*2.                                                    00015400
```

```
      DIA(I)=10.*DN(I)                                                  00015500
   65 CONTINUE                                                          00015600
C                                                                       00015700
C     CALCULATE THE GAS CONDUCTIVITY AND DENSITY IN EACH LAYER          00015800
C                                                                       00015900
      DO 70 I=1,3                                                       00016000
      AK(I)=1.051E-07*Y(I)+7.118E-05                                    00016100
      RHG(I)=28./82.6/(Y(I)+273.)                                       00016200
   70 CONTINUE                                                          00016300
C                                                                       00016400
C     CALCUATE THE NEW VOLUMES - GET COMPOSITE DENSITY                  00016500
C                                                                       00016600
      DO 55 I=1,3                                                       00016700
      RHC(I)=((VIN(I)-AM(I)/RHOD)*RHG(I)+AM(I))/VIN(I)                  00016800
      P(I)=(RHOD-RHC(I))/(RHOD-RHG(I))                                  00016900
      IF(P(I).LT.0.0)P(I)=0.0                                           00017000
      AKC(I)=((AK(I)/AKS(I)*P(I)**.667+1.-P(I)**.667)/                  00017100
     !(AK(I)/AKS(I)*(P(I)**.667-P(I))+1.-P(I)**.667+P(I)))*AKS(I)       00017200
   55 CONTINUE                                                          00017300
C                                                                       00017400
C     CALCULATE THE HEAT TRANSFERRED                                    00017500
C                                                                       00017600
      QCS=3.14159*DN(1)**2*ANU*AKG/DN(1)*(TG-Y(1))                      00017700
      QRS=3.14159*DN(1)**2*EM*F*1.35E-12*((TR+273.)**4-                 00017800
     !(Y(1)+273.)**4)                                                   00017900
      QSS=4*3.14159*AKC(2)*RN(1)*RN(2)/(RN(1)-RN(2))*(Y(1)-Y(2))        00018000
      QPS=B(1)*HP                                                       00018100
      QSM=4*3.14159*AKC(3)*RN(2)*RN(3)/(RN(2)-RN(3))*(Y(2)-Y(3))        00018200
      QPM=B(2)*HP                                                       00018300
      QPI=B(3)*HP                                                       00018400
C                                                                       00018500
C     CALCULATE THE DERIVATIVES                                         00018600
C                                                                       00018700
      YPRIME(1)=1/(AM(1)*CPS(1))*(QCS+QRS-QSS+QPS)                      00018800
      YPRIME(2)=1/(AM(2)*CPS(2))*(QSS-QSM+QPM)                          00018900
      YPRIME(3)=1/(AM(3)*CPS(3))*(QSM+QPI)                              00019000
      RETURN                                                            00019100
      END                                                               00019200
```

```
BLDTA

 .0150
 .650
 25.0
 1667.
 750.0
 627.0
```

APPENDIX 6. SULFUR RELEASE PROGRAM.

The program SULREL, listed below calculates the amount of sulfur released from a pyrolyzing black liquor drop as a function of the drop's sulfur content, physical parameters, and the heating environment to which it is exposed. The inputs to the model are included in the data file BLSDTA, and are as follows:

Drop's Dry Weight (grams)

Drop's Solids Content (fraction)

Drop's Swelling Parameter (cc/g solids)

Drop's Thiosulfate Content (fraction of solids as sulfur)

Drop's Sulfide Content (fraction of solids as sulfur)

Gas Velocity (cm/sec)

Gas Temperature (^{o}C)

Radiant Source Temperature (^{o}C)

SULREL

```
$RESET FREE                                                              00000100
FILE  1(KIND=DISK,TITLE="BLSDTA",FILETYPE=8)                             00000200
FILE  5(KIND=REMOTE,MYUSE=IN)                                            00000300
FILE  6(KIND=REMOTE,MYUSE=OUT )                                          00000400
FILE  8(KIND=PRINTER)                                                    00000500
$INCLUDE "*IMSL/DVERK"                                                   00000600
$INCLUDE "*IMSL/UERIST"                                                  00000700
$INCLUDE "*IMSL/UGETIO"                                                  00000800
$INCLUDE "*IMSL/USPKD"                                                   00000900
C                                                                        00001000
C     PROGRAM TO DETERMINE THE TEMPERATURE OF A 3-LAYER BLACK LIQUOR     00001100
C     DROPLET DURING PYROLYSIS.  THE PROGRAM ASSUMES LINEAR SWELLING     00001200
C     BETWEEN 250-500 C.                                                 00001300
C                                                                        00001400
      EXTERNAL FCN                                                       00001500
      DIMENSION Y(9),C(24),W(9,9),Y0(3),YT(3),YS(3)                      00001600
      COMMON FM(3),DIA(3),AML0(3),R(3),ANU,AKG,TG,EM,F,                  00001700
     !TR,HP,S0,SR,SW,RHO,V0(3),ROD(3),VOD(3),RHOD                        00001800
C                                                                        00001900
C     READ THE DATA FILE                                                 00002000
C                                                                        00002100
      READ(1,/) AM0,S0,SW,THI0,SUL,VEL,TG,TR                             00002200
C                                                                        00002300
C     CALCULATE DROPLET DIMENSIONS-USE EQUAL MASS LAYERS                 00002400
C                                                                        00002500
      RHO=1.0+.4137*S0+4.0715E-2*S0**2                                   00002600
      WM0=AM0/S0-AM0                                                     00002700
      R(1)=((AM0+WM0)*3./(4.*RHO*3.14159))**.33333                       00002800
      R(2)=(2./3.*(AM0+WM0)*3./(4.*RHO*3.14159))**.33333                 00002900
      R(3)=(1./3.*(AM0+WM0)*3./(4.*RHO*3.14159))**.33333                 00003000
      DO 15 I=1,3                                                        00003100
      AML0(I)=AM0/3.                                                     00003200
      V0(I)=4./3.*3.14159*R(I)**3                                        00003300
      ROD(I)=R(I)*1.5                                                    00003400
      VOD(I)=4./3.*3.14159*ROD(I)**3                                     00003500
   15 CONTINUE                                                           00003600
      RHOD=AML0(3)/VOD(3)                                                00003700
      SR=.82-.0003*TG                                                    00003800
      TGK=TG+273.                                                        00003900
C                                                                        00004000
C     CALCULATE GAS FLOW PARAMETERS                                      00004100
C                                                                        00004200
      RHOG=.341/TGK                                                      00004300
      VISC=3.255E-07*TG+1.887E-04                                        00004400
      RE=R(1)*2*VEL*RHOG/VISC                                            00004500
      CPG=4.417E-05*TG+.2504                                             00004600
      AKG=1.051E-07*TG+7.118E-05                                         00004700
      PR=CPG*VISC/AKG                                                    00004800
      ANU=2.+.6*RE**.5*PR**.3333                                         00004900
C                                                                        00005000
```

```
C     CALCULATE THE DRYING LOAD, HEAT SUPPLIED, AND TIME TO DRY          00005100
C                                                                        00005200
      DOD=ROD(1)*2.                                                      00005300
      QDRY=35.00*AMO+554.73*WMO                                          00005400
      QC=3.14159*DOD**2*ANU*AKG/DOD*(TG-150.)                            00005500
      QR=3.14159*DOD**2*.9*1.35E-12*((TR+273.)**4-3.20156E10)            00005600
      TTD=QDRY/(QC+QR)*10.                                               00005700
C                                                                        00005800
C     SET THE INITIAL CONDITIONS.  CALL THE ROUTINE DVERK TO CALCULATE   00005900
C     THE TEMPERATURES.  PRINT THE RESULTS.                              00006000
C                                                                        00006100
      NW=9                                                               00006200
      N=9                                                                00006300
      X=0.0                                                              00006400
      Y(1)=150.                                                          00006500
      Y(2)=150.                                                          00006600
      Y(3)=150.                                                          00006700
      Y(4)=0.0                                                           00006800
      Y(5)=0.0                                                           00006900
      Y(6)=0.0                                                           00007000
      Y(7)=0.0                                                           00007100
      Y(8)=0.0                                                           00007200
      Y(9)=0.0                                                           00007300
      SREL=0.0                                                           00007400
      TOL=.01                                                            00007500
      IND=1                                                              00007600
      XE=0.0                                                             00007700
      DO 25 I=1,3                                                        00007800
      DIA(I)=R(I)*20.                                                    00007900
      FM(I)=AML0(I)*1000.                                                00008000
      Y0(I)=100.0                                                        00008100
      YT(I)=0.0                                                          00008200
      YS(I)=0.0                                                          00008300
   25 CONTINUE                                                           00008400
      WRITE(8,101)                                                       00008500
  101 FORMAT(1X,"   TIME   TS     TM     TI     MS     MM     ",        00008600
     !"MI     DS     DM     DI     SUL",/,1X,"   (SEC)  (C)    (C)    ", 00008700
     !"(C)    (MG)   (MG)   (MG)   (MM)   (MM)   (MM)   (MG)")          00008800
      WRITE(8,102)XE,Y0(1),Y0(2),Y0(3),FM(1),FM(2),FM(3),                00008900
     !DIA(1),DIA(2),DIA(3),SREL                                          00009000
  102 FORMAT(1X,10F7.2,F7.4)                                             00009100
      DO 80 NO=1,400                                                     00009200
      TNO=NO*1.                                                          00009300
      DIA(1)=ROD(1)*20.                                                  00009400
      DIA(2)=ROD(2)*20.                                                  00009500
      DIA(3)=ROD(3)*20.                                                  00009600
      IF(TNO.LE.TTD)GO TO 50                                             00009700
      XEND=(TNO-TTD)/10.                                                 00009800
      CALL DVERK(N,FCN,X,Y,XEND,TOL,IND,C,NW,W,IER)                      00009900
      IF(IND.LT.0.OR.IER.GT.0)GO TO 10                                   00010000
      DO 63 I=1,3                                                        00010100
      J=I+3                                                              00010200
```

```
      K=I+6                                                              00010300
      IF(Y(J).GT.YT(I))YT(I)=Y(J)                                        00010400
      IF(Y(K).GT.YS(I))YS(I)=Y(K)                                        00010500
   63 CONTINUE                                                           00010600
   50 SREL=((YT(1)+YT(2)+YT(3))*THIO/3.+(YS(1)+YS(2)+YS(3))*             00010700
     !SUL/3.)*AMO*1000.                                                 00010800
      IF(AMOD(TNO,10.).NE.0.0)GO TO 80                                   00010900
      TINO=TNO/10.                                                       00011000
      WRITE(8,102)TINO,Y(1),Y(2),Y(3),FM(1),FM(2),FM(3),                 00011100
     !DIA(1),DIA(2),DIA(3),SREL                                          00011200
   80 CONTINUE                                                           00011300
      GO TO 20                                                           00011400
C                                                                        00011500
C     CHECK FOR ERRORS                                                   00011600
C                                                                        00011700
   10 WRITE(6,103)                                                       00011800
  103 FORMAT(1X," ERROR DETECTED!")                                      00011900
      WRITE(6,104)IND,IER                                                00012000
  104 FORMAT(1X,"IND= ",I3," IER= ",I3)                                  00012100
   20 STOP                                                               00012200
      END                                                                00012300
C                                                                        00012400
C     SUBROUTINE FUNCTION TO CALCULATE THE DIFFERENTIAL EQUATION         00012500
C                                                                        00012600
      SUBROUTINE FCN(N,X,Y,YPRIME)                                       00012700
      COMMON FM(3),DIA(3),AMLO(3),R(3),ANU,AKG,TG,EM,F,                  00012800
     !TR,HP,SO,SR,SW,RHO,VO(3),ROD(3),VOD(3),RHOD                        00012900
      REAL X,Y(9),YPRIME(9),DN(3),RN(3),AK(3),RHG(3),VIN(3),             00013000
     !CPS(3),AKS(3),B(3),AM(3),RHC(3),P(3),AKC(3),PSC(3),                00013100
     !AKEQT(3),AKEQS(3),CLAMP(3)                                         00013200
      INTEGER N                                                          00013300
C                                                                        00013400
C     CALCULATE TEMPERATURE-DEPENDENT BLACK LIQUOR PARAMETERS AND        00013500
C     THE HEAT TRANSFER TERMS                                            00013600
C                                                                        00013700
      F=1.0                                                              00013800
      EM=.75                                                             00013900
      DO 35 I=1,3                                                        00014000
      HP=-150.0                                                          00014100
      CPS(I)=0.7                                                         00014200
      AKS(I)=5.E-06*Y(I)-2.E-4                                           00014300
      B(I)=(1.1365+.2065/(R(1)*2.)-4.0625*SO+5.062E-03*Y(I))*            00014400
     !AMLO(I)/100.                                                       00014500
      IF(B(I).LT.0.0)B(I)=0.0                                            00014600
      IF(Y(I).LT.250.)B(I)=0.0                                           00014700
      AM(I)=AMLO(I)-B(I)*X                                               00014800
      PSR=AM(I)/AMLO(I)                                                  00014900
      IF(PSR.GT.SR)GO TO 45                                              00015000
      AM(I)=AMLO(I)*SR                                                   00015100
      B(I)=0.0                                                           00015200
   45 FM(I)=AM(I)*1000.                                                  00015300
   35 CONTINUE                                                           00015400
```

```
C                                                                       00015500
C     CALCULATE THE NEW RADII AND DIAMETERS                             00015600
C                                                                       00015700
      DVOL= SW*AMLO(3)-VOD(3)                                           00015800
      DO 60 I=1,3                                                       00015900
      PSC(I)=(Y(I)-250.)/250.                                           00016000
      IF(PSC(I).GT.1.)PSC(I)=1.                                         00016100
      IF(PSC(I).LT.0.)PSC(I)=0.                                         00016200
      VIN(I)=PSC(I)*DVOL+VOD(3)                                         00016300
   60 CONTINUE                                                          00016400
      RN(3)=(VIN(3)*3./(4.*3.14159))**.33333                            00016500
      RN(2)=((VIN(3)+VIN(2))*3./(4.*3.14159))**.33333                   00016600
      RN(1)=((VIN(3)+VIN(2)+VIN(1))*3./(4.*3.14159))**.33333            00016700
      DO 65 I=1,3                                                       00016800
      DN(I)=RN(I)*2.                                                    00016900
      DIA(I)=10.*DN(I)                                                  00017000
   65 CONTINUE                                                          00017100
C                                                                       00017200
C     CALCULATE THE GAS CONDUCTIVITY AND DENSITY IN EACH LAYER          00017300
C                                                                       00017400
      DO 70 I=1,3                                                       00017500
      AK(I)=1.051E-07*Y(I)+7.118E-05                                    00017600
      RHG(I)=28./82.6/(Y(I)+273.)                                       00017700
   70 CONTINUE                                                          00017800
C                                                                       00017900
C     CALCUATE THE NEW VOLUMES - GET COMPOSITE DENSITY                  00018000
C                                                                       00018100
      DO 55 I=1,3                                                       00018200
      RHC(I)=((VIN(I)-AM(I)/RHOD)*RHG(I)+AM(I))/VIN(I)                  00018300
      P(I)=(RHOD-RHC(I))/(RHOD-RHG(I))                                  00018400
      IF(P(I).LT.0.0)P(I)=0.0                                           00018500
      AKC(I)=((AK(I)/AKS(I)*P(I)**.667+1.-P(I)**.667)/                  00018600
     !(AK(I)/AKS(I)*(P(I)**.667-P(I))+1.-P(I)**.667+P(I)))*AKS(I)       00018700
   55 CONTINUE                                                          00018800
C                                                                       00018900
C     CALCULATE THE HEAT TRANSFERRED                                    00019000
C                                                                       00019100
      QCS=3.14159*DN(1)**2*ANU*AKG/DN(1)*(TG-Y(1))                      00019200
      QRS=3.14159*DN(1)**2*EM*F*1.35E-12*((TR+273.)**4-                 00019300
     !(Y(1)+273.)**4)                                                   00019400
      QSS=4*3.14159*AKC(2)*RN(1)*RN(2)/(RN(1)-RN(2))*(Y(1)-Y(2))        00019500
      QPS=B(1)*HP                                                       00019600
      QSM=4*3.14159*AKC(3)*RN(2)*RN(3)/(RN(2)-RN(3))*(Y(2)-Y(3))        00019700
      QPM=B(2)*HP                                                       00019800
      QPI=B(3)*HP                                                       00019900
      DO 62 I=1,3                                                       00020000
      AKEQT(I)=EXP(3733./(Y(I)+273.)-4.957)                             00020100
      AKEQS(I)=EXP(7497./(Y(I)+273.)-9.785)                             00020200
      IF(AKEQT(I).GT.1.0)AKEQT(I)=1.0                                   00020300
      IF(AKEQS(I).GT.1.0)AKEQS(I)=1.0                                   00020400
      CLAMP(I)=1.0                                                      00020500
      IF(Y(I).LT.250.)CLAMP(I)=0.0                                      00020600
```

```
   62 CONTINUE                                                          00020700
C                                                                       00020800
C     CALCULATE THE DERIVATIVES                                         00020900
C                                                                       00021000
      YPRIME(1)=1/(AM(1)*CPS(1))*(QCS+QRS-QSS+QPS)                      00021100
      YPRIME(2)=1/(AM(2)*CPS(2))*(QSS-QSM+QPM)                          00021200
      YPRIME(3)=1/(AM(3)*CPS(3))*(QSM+QPI)                              00021300
      DO 61 I=1,3                                                       00021400
      J=I+3                                                             00021500
      K=I+6                                                             00021600
      YPRIME(J)=CLAMP(I)*255.1*EXP(-10.49/1.987E-03/                    00021700
     !(Y(I)+273.))*(AKEQT(I)*.4339-Y(J))                                00021800
      YPRIME(K)=CLAMP(I)*9692470.*EXP(-24.01/1.987E-03/                 00021900
     !(Y(I)+273.))*(AKEQS(I)*.4020-Y(K))                                00022000
   61 CONTINUE                                                          00022100
      RETURN                                                            00022200
      END                                                               00022300
```

BLSDTA

```
 .0200
 .700
 50.0
 .0000
 .0300
  .49
 666.
 666.
```

APPENDIX 7. TESTS OF PYROLYSIS KINETICS REACTOR

Uniformity of Heating on Wire Screen

The uniformity of temperature on various parts of the wire screen on which the liquor samples were heated was tested. The screen was divided into twenty-five sections (a five by five grid). A bare wire thermocouple (type K, .005" diameter) was placed on each grid section and the reactor's heating circuit activated. The maximum temperature obtained was recorded. Table 34 shows the results of these tests. The results obtained indicate that the temperature on the screen is reasonably uniform.

Table 33. Temperature profile of pyrolysis reactor screen. Average of five tests ± 95% confidence limits Temperature in °C

Long Dimension					
446 ± 24	468 ± 10	454 ± 30	443 ± 29	454 ± 35	Narrow Dim
478 ± 19	448 ± 11	464 ± 11	471 ± 14	464 ± 17	
460 ± 17	467 ± 11	477 ± 20	482 ± 12	456 ± 14	
475 ± 6	456 ± 11	447 ± 27	460 ± 15	458 ± 17	
460 ± 17	441 ± 6	444 ± 6	448 ± 20	454 ± 17	

Test for Reaction of Sulfur Gases With Wire Screen

It is necessary that the sulfur-containing pyrolysis products do not react with the wire screen during pyrolysis. To insure that no reaction was taking place, pyrolysis tests were run comparing sulfur releases from a kraft liquor pyrolyzed on untreated wire screens to releases obtained when the same liquor was pyrolyzed on screens that had been passivated by gold plating them. The results of these tests, listed in Table 35, show no evidence of

significant reaction of the sulfur gases with the wire.

Table 34. Test for reaction of released sulfur with wire screen.

Untreated Wire		Gold-plated Wire	
Temp. (°C)	Sulfur Released (mg S/100 g solids)	Temp. (°C)	Sulfur Released (mg S/100 g solids)
496	756	511	1607
493	1128	502	1283
517	1906	458	1355
482	964	499	1149
487	1606	511	1207
482	811	490	945
493	1255	490	1260
470	1395	467	1610
487	1511	476	1564
511	1995	502	1695
511	1275	517	1052
496	1661	511	886
520	1935	499	1341
476	1375	523	1687
523	1123	487	1480
Ave. 496	1380 ± 217	496	1341 ± 146

Effect of Pyrolysis Heating Rate

The effect that using different heating rates to reach the final temperature had on the amount of sulfur released during the pyrolysis kinetics experiments was examined. Samples of the liquor containing thiosulfate were pyrolyzed using two different heating rates (3973° C/sec, and 2305° C/sec) and the amounts of sulfur released were compared. The results of these tests, shown in Table 36, show that there is no significant heating rate effect.

Table 35. Effect of different heating rates on sulfur release. Thiosulfate-containing liquor; 9.0 seconds pyrolysis time

Heating Rate (°C/sec)	Final Temp. (°C)	Sulfur Released (mg S/100 g solids)
3973	440	996
	422	909
	458	959
	431	960
	422	946
	434	1059
	452	864
Ave.	437	956 ± 57
2305	434	918
	461	945
	434	851
	452	808
	428	1007
	428	1000
	428	840
Ave.	438	910 ± 91